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December 5, 2005

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PATENT APPLICATION
3M Case No. 59678US002
HBSR Docket No. 1571.0246-000

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GREGORY MILLS
QUALITY ASSURANCE SPECIALIST

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Applicants:	Dennis J. Chirhart, Mark A. Young, and Steven B. Kelley		
Application No.	10/815,366	Group Art Unit: 1772	
Filed:	April 1, 2004	Examiner: Ahmad, Nassar	
Confirmation No.:			
Title:	Retroreflective Sheeting with Controlled Cap-Y		

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December 5, 2005 — Marianne Lentini
Date — Signature

MARIANNE LENTINI
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Third-Party Submission in Published Application under 37 C.F.R. § 1.99

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

This Third-Party Submission in Published Application under 37 C.F.R. § 1.99 is submitted for the above-referenced application, which was published for United States Patent Application 20050221042 A1 on October 6, 2005 naming Dennis J. Chirhart *et al.* as inventors. The publication identified 3M Innovative Properties Company as the assignee.

This submission under 37 C.F.R. § 1.99 is filed within two months from the date of publication of the application (Sec. 1.215(a)) and prior to the mailing of a notice of allowance (Sec. 1.311).

The undersigned has identified the following publications as relevant to the prosecution of the above-referenced application. The undersigned requests that the following publications be considered:

12/08/2005 EAREGAY1 00000049 10815366

01 FC:1806 180.00 OP

_____ U.S. Patent 6,481,857 B2, issued on November 19, 2002 to Peter R. Smith;

_____ U.S. Patent 6,323,266 B2, issued on November 27, 2001 to Edward D. Phillips

_____ U.S. Patent 5,508,105 A, issued on April 16, 1996 to Bruce D. Orensteen *et al.*;

_____ U.S. Patent 4,801,193, issued on January 31, 1989 to David C. Martin; and

_____ U.S. Patent 4,153,412, issued on May 8, 1979 to Terry R. Bailey.

____________________ ____________________

Examiner Date

It is requested that the information disclosed herein be made of record in this application. Copies of the cited references are enclosed.

The undersigned requests that the Third-Party Submission and cited references be reviewed and considered by the Examiner. The fee set forth in 37 C.F.R. § 1.17(p) as required under 37 C.F.R. 1.99(b)(1) is included in the form of a check for $180.00 is enclosed. A copy of this Statement is enclosed for accounting purposes. Please charge any deficiency in fees and credit any overpayment to Deposit Account 08-0380.

Respectfully submitted,

HAMILTON, BROOK, SMITH & REYNOLDS, P.C.

Robert T. Conway

Robert T. Conway
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Dated: December 5, 2005
Concord, Massachusetts 01742-9133

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I hereby certify that a true copy of the forgoing Third-Party Submission in Published Application under 37 C.F.R. § 1.99 with each of the cited U.S. patents has been mailed this fifth day of December, 2005 by first-class mail, postage prepaid, to:

3M Innovative Properties Company
P.O. Box 33427
St. Paul, Minnesota 55133-3427

Robert T. Conway

Robert T. Conway

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PATENT APPLICATION
3M Case No. 59678US002
HBSR Docket No. 1571.0246-000

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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Application No.	10/815,366	Group Art Unit: 1772
Filed:	April 1, 2004	Examiner: Ahmad, Nassar
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Dated: December 5, 2005
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US006481857B2

(12) **United States Patent**
Smith

(10) **Patent No.: US 6,481,857 B2**
(45) **Date of Patent: *Nov. 19, 2002**

(54) **PERFORATED RETROREFLECTIVE FILM**

(75) Inventor: **Peter R. Smith**, Avon, CT (US)

(73) Assignee: **Reflexite Corporation**, Avon, CT (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 41 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **09/730,522**

(22) Filed: **Dec. 5, 2000**

(65) **Prior Publication Data**

US 2001/0017731 A1 Aug. 30, 2001

Related U.S. Application Data

(63) Continuation-in-part of application No. 09/211,962, filed on Dec. 15, 1998, now Pat. No. 6,155,689.
(60) Provisional application No. 60/069,818, filed on Dec. 16, 1997.

(51) **Int. Cl.**^{7} **G02B 5/122**
(52) **U.S. Cl.** **359/530**; 359/529; 359/533; 359/833; 359/834
(58) **Field of Search** 359/530, 529, 359/531, 532, 533, 833, 834; 428/137, 913.3

(56) **References Cited**

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5,939,168	A	8/1999	Andriash	428/138
6,155,689	A	12/2000	Smith	359/530

* cited by examiner

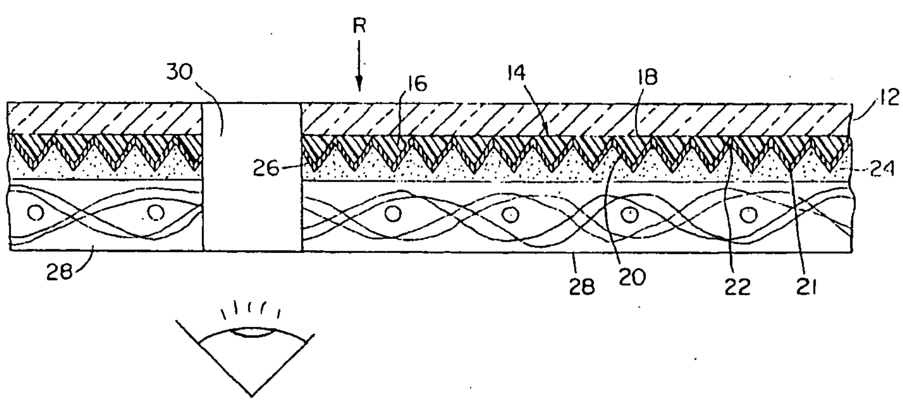
Primary Examiner—Cassandra Spyrou
Assistant Examiner—Leo Boutsikaris
(74) *Attorney, Agent, or Firm*—Hamilton, Brook, Smith & Reynolds, P.C.

(57) **ABSTRACT**

A see-through retroreflective structure includes a transparent polymeric film, an array of retroreflective elements attached to the polymeric film, and an array of apertures through the retroreflective structure within the array of retroreflective elements. In one embodiment, the retroreflective structure includes a metalized reflective layer formed on the transparent prism elements and a support layer, such as a fabric, is attached to the metalized reflective layer.

The method includes providing a transparent polymeric film. An array of retroreflective elements is attached to the polymeric film. The array of retroreflective elements and the transparent polymeric film are perforated through the retroreflective structure to form an array of apertures, thereby forming a retroreflective structure. The apertures are of sufficient size and spacing to provide a see-through capability. In one embodiment, a metalized reflective layer can be applied to the retroreflective elements and a support layer, such as a fabric, is attached to the metalized reflective layer.

44 Claims, 11 Drawing Sheets



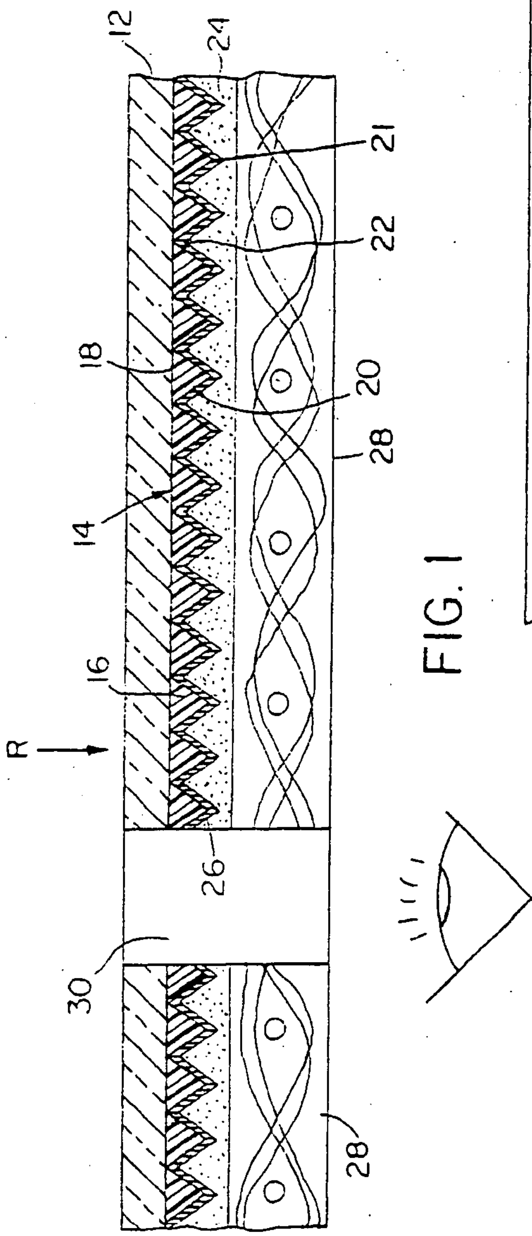
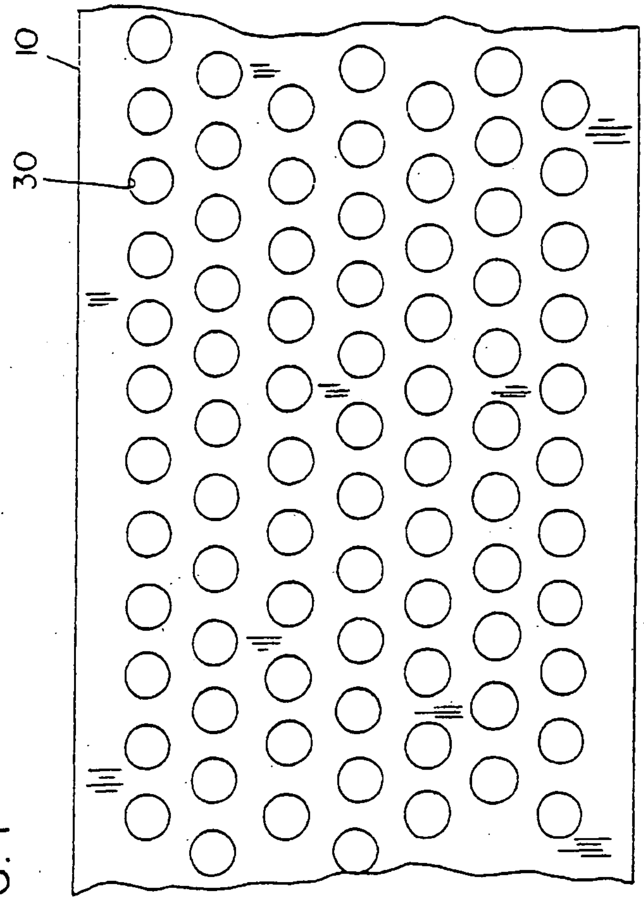


FIG. 1



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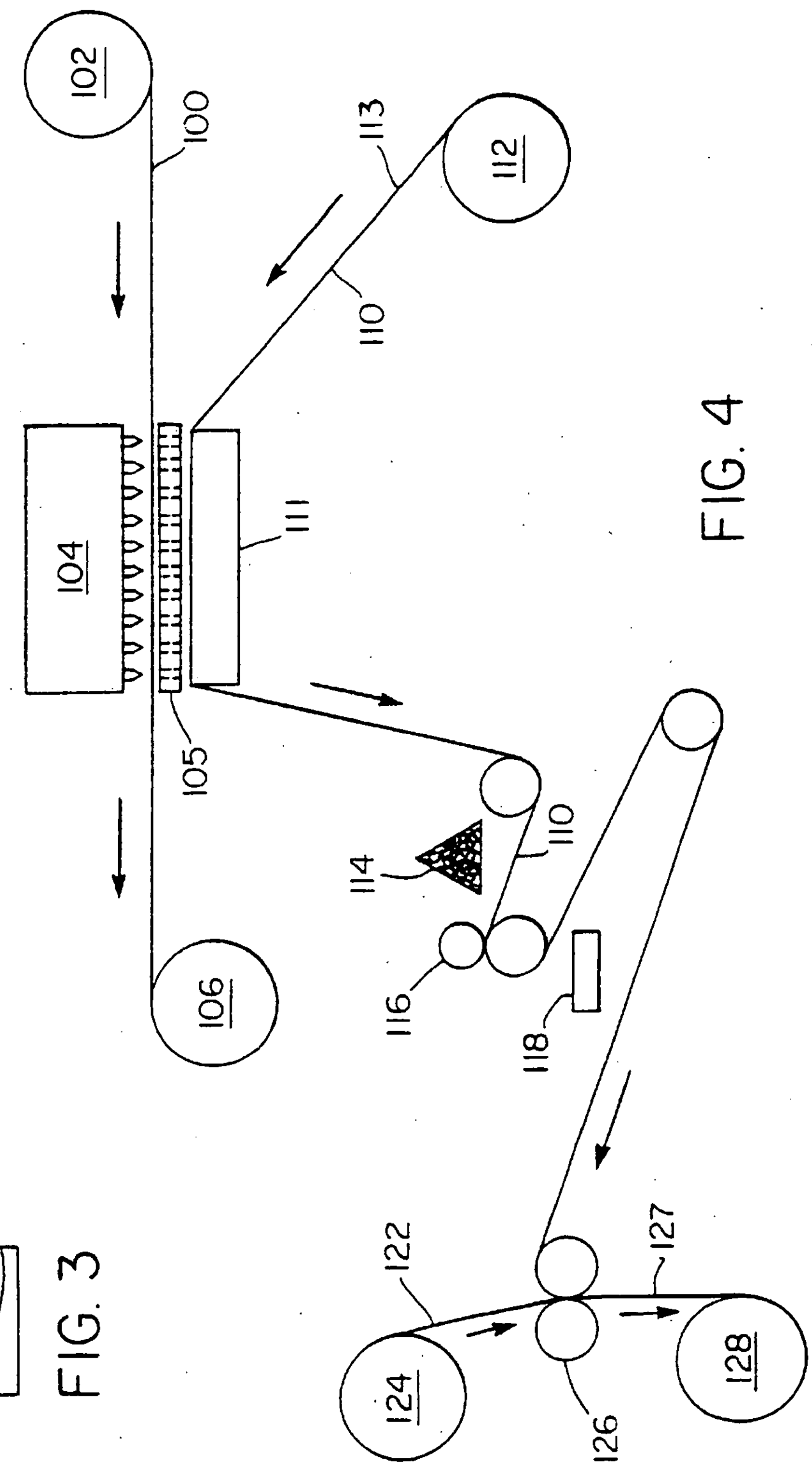

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FIG. 4

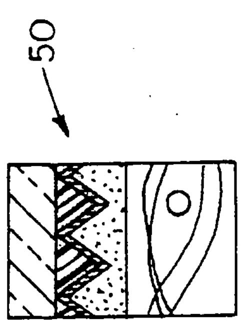

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FIG. 3

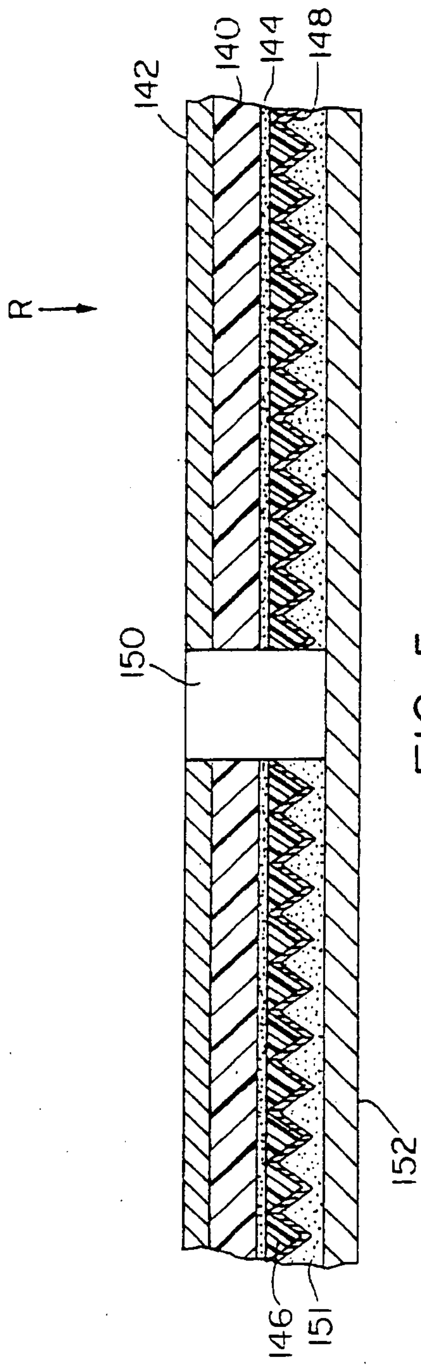
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FIG. 5

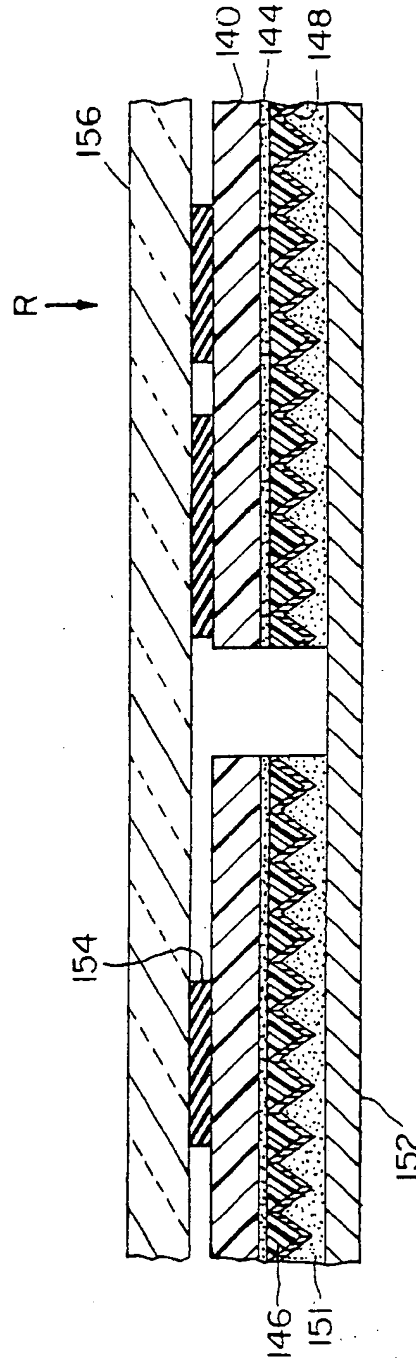
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FIG. 6

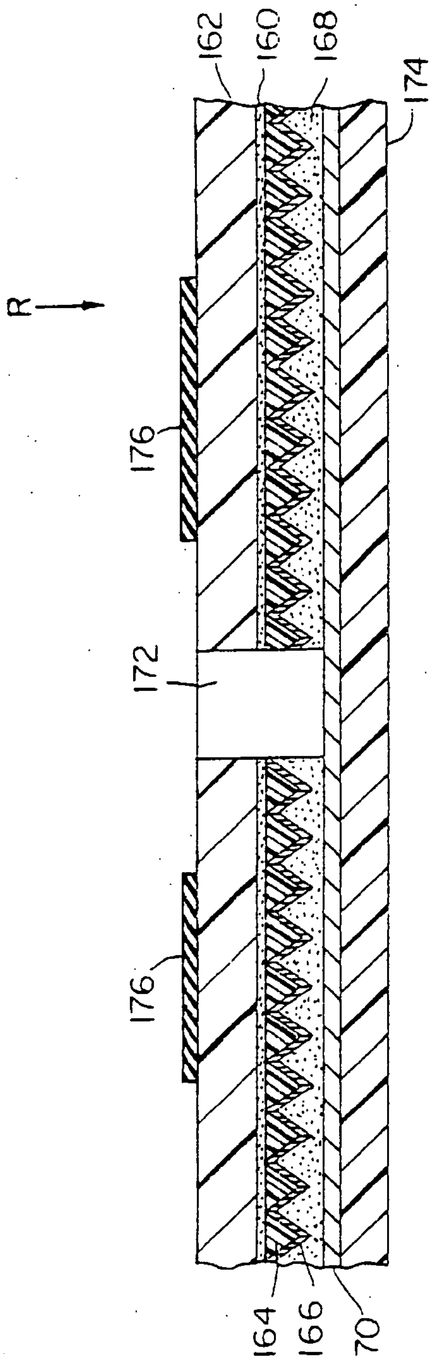
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FIG. 7

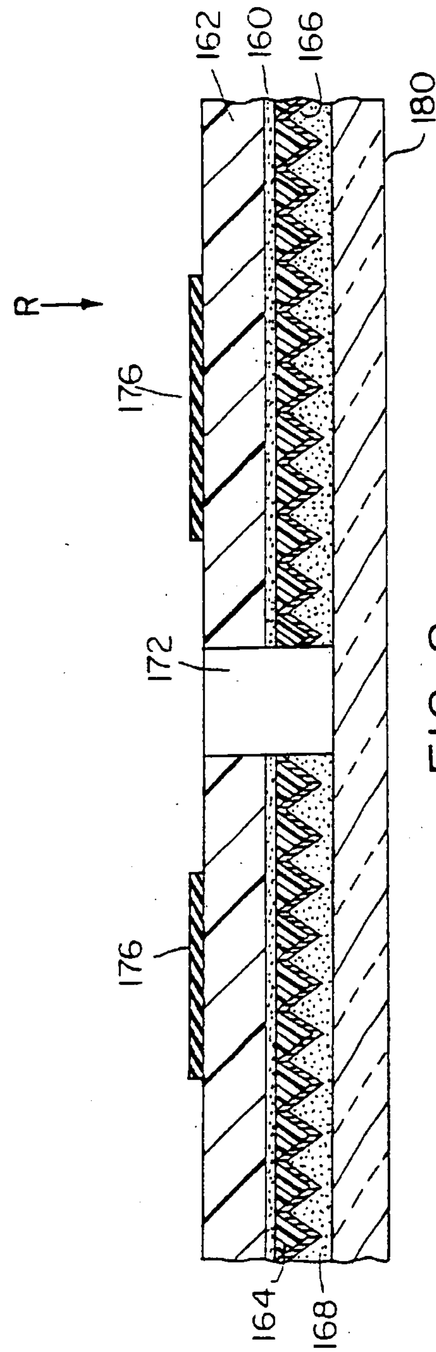
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FIG. 8

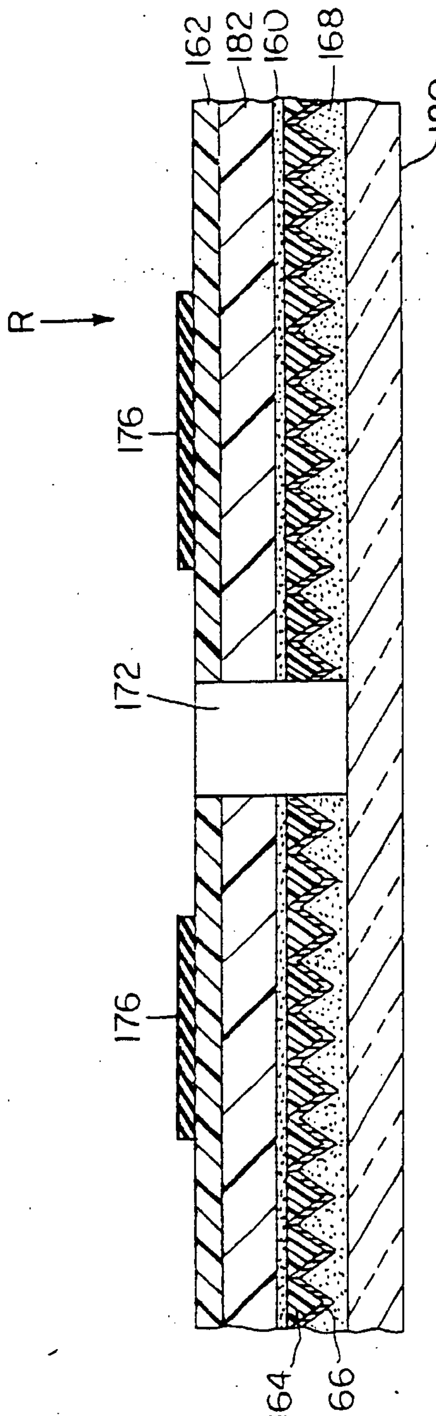
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FIG. 9

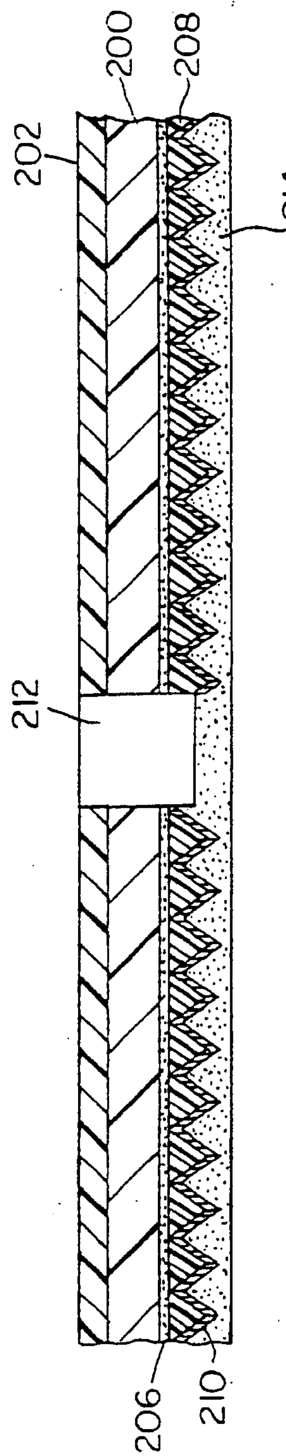
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FIG. 10

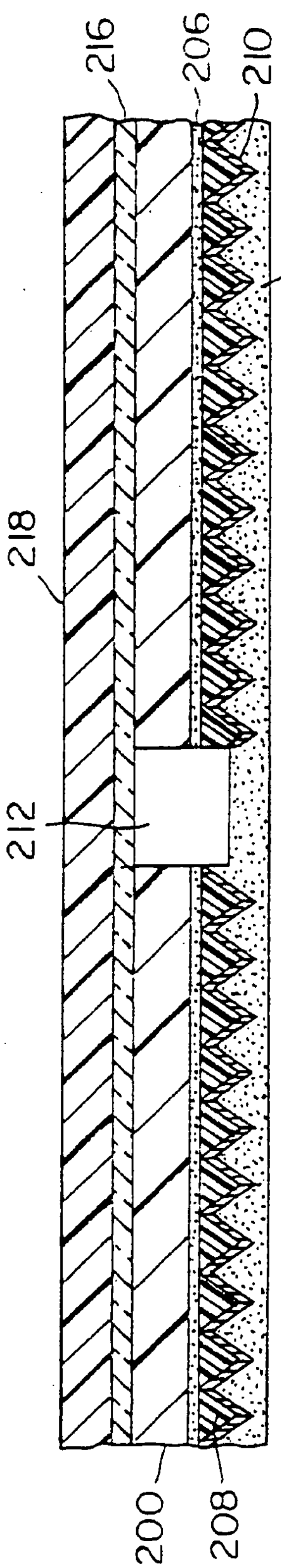

FIG. 11

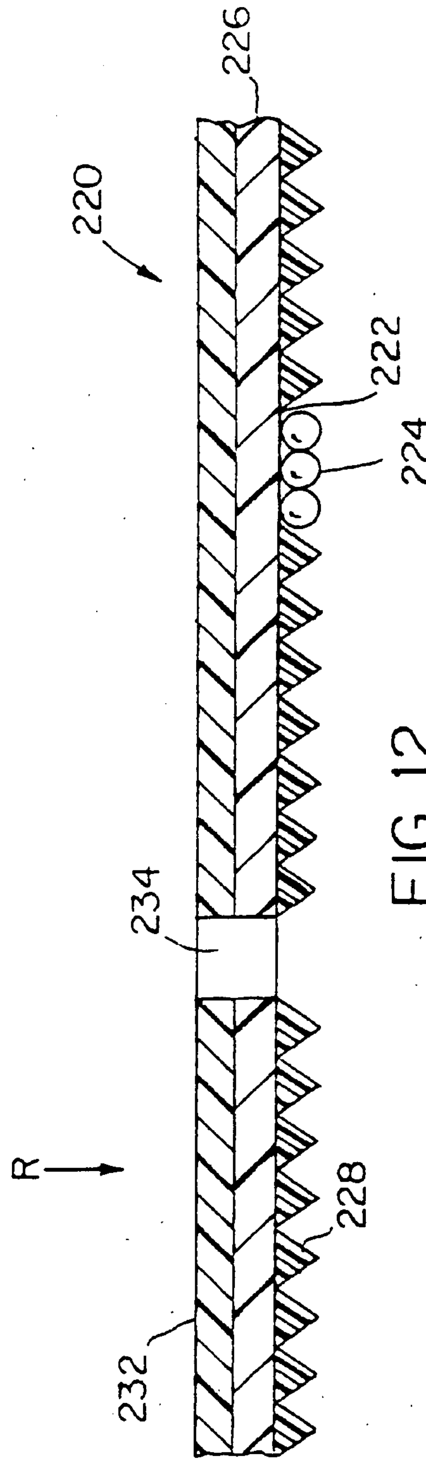

FIG. 12

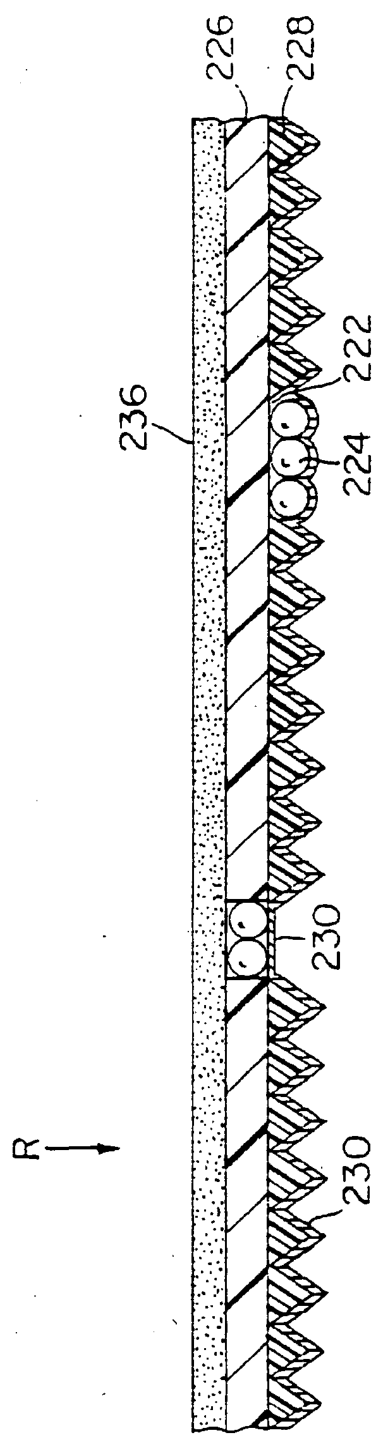
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FIG. 13

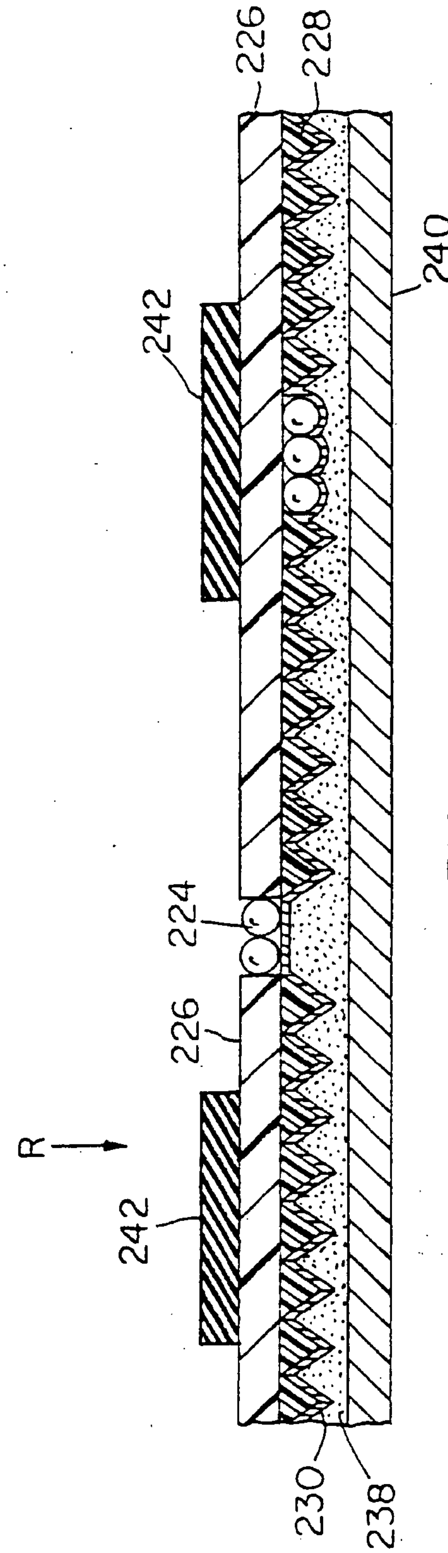
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FIG. 14

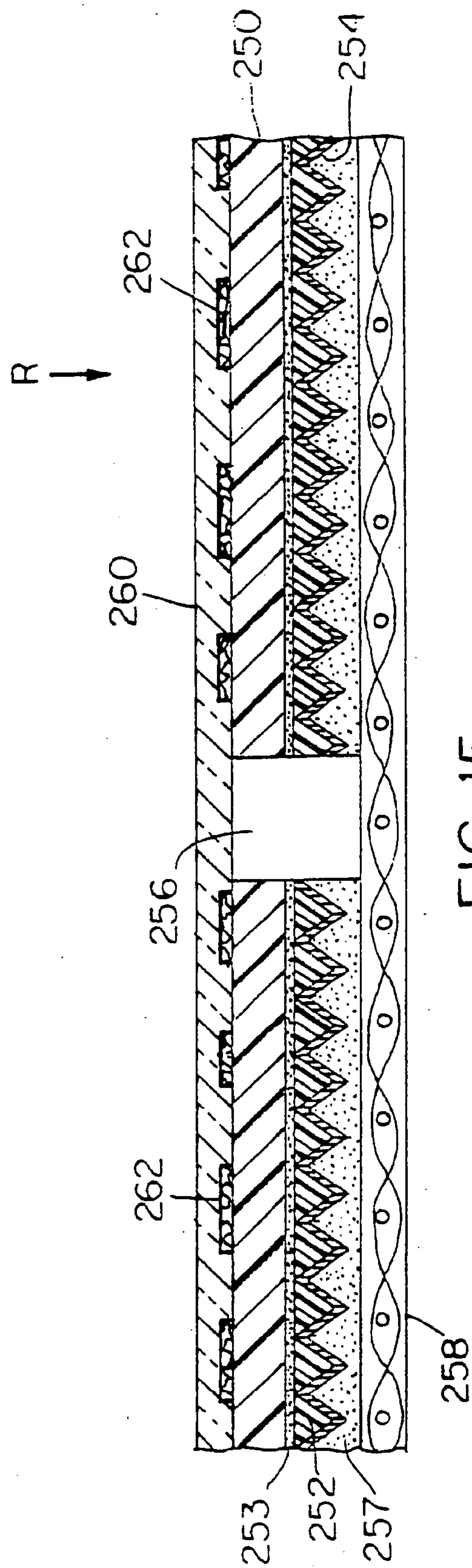

FIG. 15

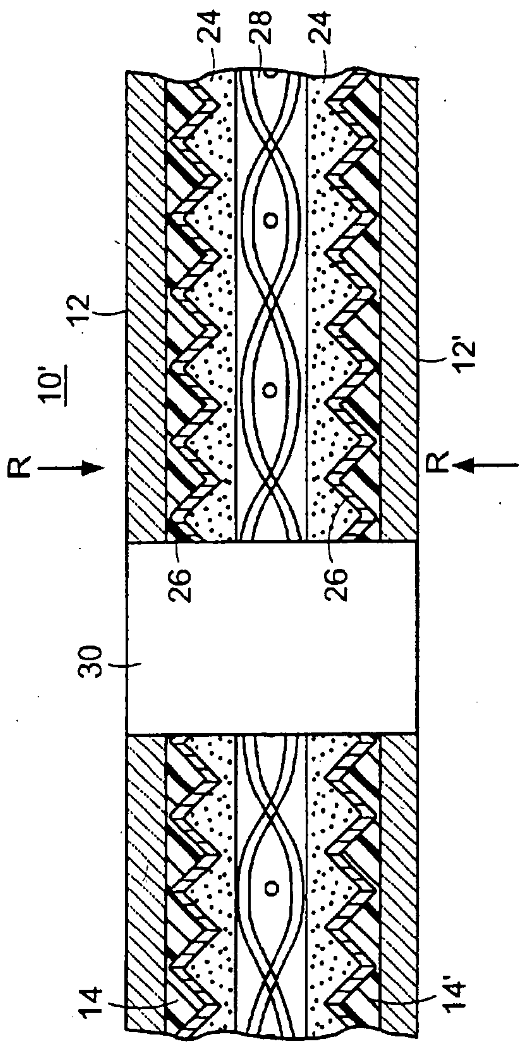

FIG. 16

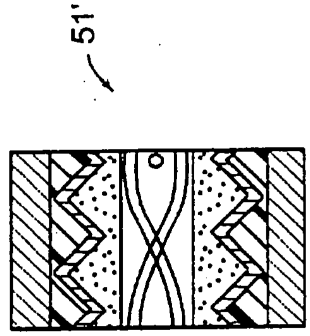

FIG. 17

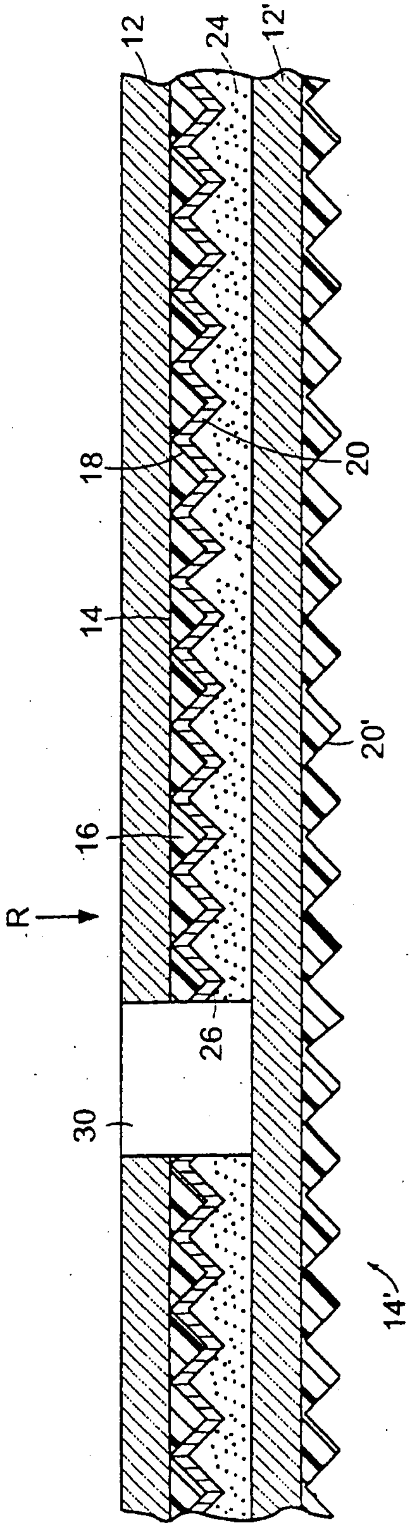

FIG. 18

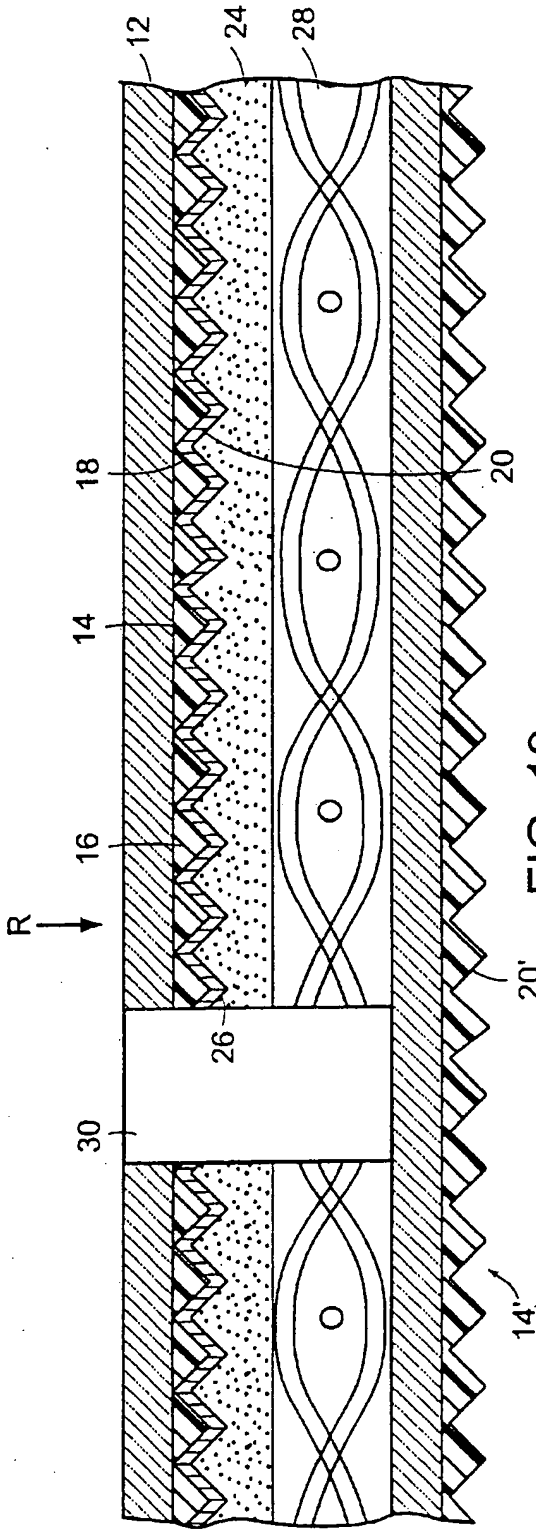

FIG. 19

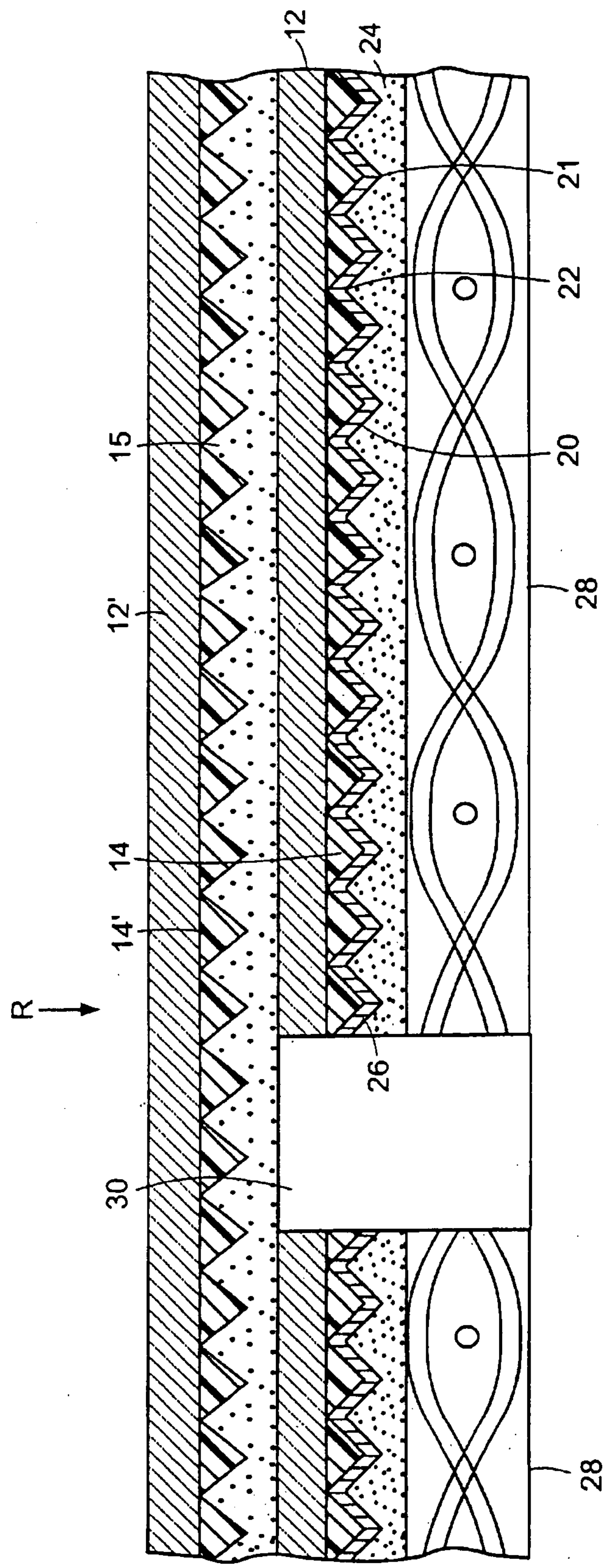

FIG. 20

PERFORATED RETROREFLECTIVE FILM

RELATED APPLICATIONS

This application is a Continuation-in-Part Application of U.S. application Ser. No. 09/211,962, filed Dec. 15, 1998, which claims the benefit of U.S. Provisional Application Ser. No. 60/069,818, filed Dec. 16, 1997. The contents of each application are incorporated herein by reference in their entirety.

BACKGROUND OF THE INVENTION

Retroreflective materials are employed for various safety and decorative purposes. Particularly, these materials are useful at night time when visibility is important under low light conditions. With perfect retroreflective materials, light rays are reflected essentially towards a light source in a substantially parallel path along an axis of retroreflectivity.

Many types of retroreflective material exist for various purposes. These retroreflective materials can be used as reflective tapes and patches for clothing, such as vests and belts. Also, retroreflective materials can be used on posts, barrels, traffic cone collars, highway signs, warning reflectors, etc. Retroreflective material can be comprised of arrays of randomly oriented micron diameter spheres or close packed cube-corner (prismatic) arrays.

Cube-corner or prismatic retroreflectors are described in U.S. Pat. No. 3,712,706, issued to Stamm on Jan. 23, 1973, the teachings of which are incorporated by reference herein. Generally, the prisms are made by forming a master negative die on a flat surface of a metal plate or other suitable material. To form the cube-corners, three series of parallel equidistance intersecting V-shaped grooves 60 degrees apart are inscribed in the flat plate. The die is then used to process the desired cube-corner array into a rigid flat plastic surface.

Further details concerning the structures and operation of cube-corner microprisms can be found in U.S. Pat. No. 3,684,348, issued to Rowland on Aug. 15, 1972, the teachings of which are incorporated by reference herein. A method for making retroreflective sheeting is also disclosed in U.S. Pat. No. 3,689,346, issued to Rowland on Sep. 5, 1972, the teachings of which are incorporated by reference herein. The disclosed method is for forming cube-corner microprisms in a cooperatively configured mold. The prisms are bonded to sheeting which is applied thereover to provide a composite structure in which the cube-corner formations project from one surface of the sheeting.

SUMMARY OF THE INVENTION

The present invention is directed to a "see-through" retroreflective structure and a method for forming the same. The see-through retroreflective structure includes a transparent polymeric film, an array of retroreflective elements attached to the polymeric film, and an array of apertures through the retroreflective structure within the array of retroreflective elements. In one embodiment, the retroreflective structure includes a metalized reflective layer formed on the retroreflective elements and a support layer, such as a fabric, is attached to the metalized reflective layer. The see-through feature of the structure allows a person inside a vehicle or building to see out a window while those viewing outside can see a graphic display on the structure during the day and night.

A retroreflective structure is also provided which includes a film having a first side and a second side, a first array of retroreflective cube-corner elements attached to the first side of the film, and an array of apertures through the retroreflective structure within the array of retroreflective cube-corner elements. A second array of retroreflective cube-corner elements is attached to the second side of the film. The apertures can be formed by removing a portion of the film and the elements.

The method includes attaching an array of retroreflective elements on a transparent polymeric film. The array of retroreflective elements and the transparent polymeric film are perforated through the retroreflective structure to form an array of apertures, thereby forming a see-through retroreflective structure. In one embodiment, a metalized reflective layer can be applied to the retroreflective elements and a support layer, such as a fabric, is attached to the metalized reflective layer.

A retroreflective particle is further provided comprising a film having a first side and a second side, a first array of retroreflective cube-corner elements attached to the first side of the film, and a second array of retroreflective cube-corner elements attached to the second side of the film.

A transflector is also provided which includes a film, an array of retroreflective cube-corner elements attached to a first side of the film, an array of apertures through the retroreflective structure within the array of retroreflective cube-corner elements, and a printed sheet attached to a second side of the film. In one embodiment, the apertures are formed by removing a portion of the film and the elements. A diffuse film can be attached to the metalized reflective layer.

The present invention can be used as trim on clothing apparel, such as running suits and running shoes. In particular, the invention can display a moiré pattern. Also, the invention can be used on windows to partially retroreflect incoming light while allowing a person to partially see through the window from the other side. Further, the invention can be used as advertising display panels on windows, as reflective sun screens for windows in automobiles, etc. Furthermore, the structure is suitable for ink jet and digital printing with a whiteness background.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a first embodiment of a retrorefective structure of the present invention.

FIG. 2 view of the first embodiment of a retroreflective structure of the present invention.

FIG. 3 is a cross-sectional view of a second embodiment of the retroreflective structure of the present invention.

FIG. 4 is a schematic diagram of a second embodiment of the method for forming the invention.

FIG. 5 is a cross-sectional view of a method for forming an alternative retroreflective structure at a first point in forming a third embodiment of the present invention.

FIG. 6 is a cross-sectional view of a method for forming an alternative retroreflective structure at a second point in forming the third embodiment of the present invention.

FIG. 7 is a cross-sectional view of a method for forming an alternative retroreflective structure at a first point in forming a fourth embodiment of the present invention.

FIG. 8 a cross-sectional view of a method for forming an alternative retroreflective structure at a second point in forming the fourth embodiment of the present invention.

FIG. 9 a cross-sectional view of a method for forming an alternative retroreflective structure at a point in forming a fifth embodiment of the present invention.

FIG. 10 is a cross-sectional view of a method for forming an alternative retroreflective structure at a point in forming a sixth embodiment of the present invention.

FIG. 11 is a cross-sectional view of a method for forming an alternative retroreflective structure at a second point in forming the sixth embodiment of the present invention.

FIG. 12 is a cross-sectional view of a method for forming an alternative retroreflective structure at a first point in forming a seventh embodiment of the present invention.

FIG. 13 is a cross-sectional view of a method for forming an alternative retroreflective structure at a second point in forming the seventh embodiment of the present invention.

FIG. 14 is a cross-sectional view of a method for forming an alternative retroreflective structure at a third point in forming the seventh embodiment of the present inventions

FIG. 15 is a cross-sectional view of a method for forming an alternative retroreflective structure at a point in forming an eighth embodiment of the present invention.

FIG. 16 is a cross-sectional view of another embodiment of a retroreflective structure of the present invention.

FIG. 17 is a cross-sectional view of yet another embodiment of the retroreflective structure of the present invention.

FIG. 18 is a cross-sectional view of another embodiment of the retroreflective structure of the present invention.

FIG. 19 is a cross-sectional view of yet another embodiment of the retroreflective structure of the present invention.

FIG. 20 is a cross-sectional view of a further embodiment of the retroreflective stature of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention, as illustrated in the accompanying drawings in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention. All percentages and parts are by eight unless otherwise indicated.

Retroreflective structure **10**, as shown in FIG. **1**, has a base film **12** that is comprised of a transparent thermoplastic film, such as polyvinyl chloride, polyvinylidene chloride, urethane films, polyfluorocarbon polymers, etc. In another embodiment, the thermoplastic is an ethylene-tetrafluoroethylene copolymer. In alternative embodiments, the base film **12** can be formed from an elastic material, such as flexible polyether urethanes which perform well in laundering and flexible polyaliphatic urethanes which perform well in outdoor environments. Base film **12** is transparent to visible light and can be either clear or colored. An example of a suitable base film **12** is a polyvinyl chloride film available from Renoliot Corp. under the trademark Renoliot™ H1W series. Base film **12** can have a thickness in the range of between about 0.001 and 0.022 inches (0.025 and 0.56 mm). In a preferred embodiment, the thickness is in the range of between about 0.008 and 0.02 inches (0.2 and 0.51 mm). The selected thickness is dependent upon the method of fabrication, such as heating, radio high frequency welding, ultrasonic welding, the thermoplastic selected, and the characteristics desired for the retroreflective structure.

The prism array **14**, which can include retroreflective cube-corner prism elements **16**, is formed on the base film **12**. Prism array **14** has a window side **18** exposed to incoming rays R and facet sides **20** and is attached on window side **18** to the base film **12**. Prism array **14** is formed of a transparent polymer. After being formed, the polymer is preferably rigid at room temperature, which is defined as being substantially inflexible. The rigidity of the polymer in the prism array allows the prism elements to retain their optical characteristics. The prism array polymer can also be non-extensible, which is defined as not being capable of being substantially stretched without breaking. The polymer is selected from a wide variety of polymers which include the polymers of urethane, acrylic acid esters, cellulose esters, ethylenically unsaturated nitriles, hard epoxy acrylates, etc. Other polymers include polycarbonates, polyesters and polyolefins, acrylated silanes, hard polyester urethane acrylates. Other polymers which are not as rigid can also be used. These include polyvinyl chloride and polyvinylidene chloride. Preferably, the polymer is cast in a prismatic mold with a monomer or oligomer polymerization initiated by ultraviolet radiation.

The prism elements **16** of the prism array **14** can be cube-corner in shape and have a length along each cube-side edge in the range of between about 0.0015 and 0.02 inches (0.038 and 0.51 mm). In one embodiment, each cube-side edge has a length of about 0.006 inches (0.15 mm). Preferably, each cube-side edge has a length of between about 0.004 and 0.008 inches (0.1 and 0.2 mm).

The thickness of prism array **14** at valley **22**, where the rigid prism elements intersect, is preferably sufficiently thin so that the prism array **14** can crack and split along the valleys **22** when a minimal force is applied to retroreflective structure **10**. In one embodiment, the thickness of prism array **14**, which is the distance from window side **18** to apex **21** of prisms, is in the range of between about 0.002 and 0.009 inches (0.05 and 0.23 mm).

The base film **12** provides a substrate for prism array **14** to provide a smooth surface upon which the prism elements can be attached. The window side **18** of the prism elements **16** is attached to the base film **12**. The prism array **14** can be laminated to the base film **12** with a transparent adhesive. Alternatively, the prism array **14** can be cast directly onto the base film **12**.

An adhesive **24** can be applied to the prism facets **20** for attaching a backing layer to the retroreflective structure. If an adhesive is employed on the prism facets, the adhesive can cause the surface of the prisms to wet, thereby destroying the air interface and eliminating the ability of the prism to retroreflect. As a result, reflective coating **26** is preferably deposited on the surface of the dihedral facets **20**. Typically, the reflective coatings are formed by sputtering aluminum, silver or gold or by vacuum metalization. Alternatively, metal lacquers, dielectric coatings and other specular coating materials can be employed.

Backing layer **28** is placed on the facet side **20** of the prism array **14**. The backing layer **28** can be formed of a thermoplastic. For instance, backing film **28** can be formed from a thermoplastic, such as a polyvinyl chloride, polyvinylidene chloride, urethane films, polyfluorocarbon polymers including an ethylene-tetrafluoroethylene copolymer, etc., which has a low temperature of distortion. The thermoplastic of backing layer **28** can be transparent to visible light and is either clear or colored. Alternatively, backing layer **28** can be a cloth or fabric, such as a polyester cloth. In one embodiment, the base film **12** and backing layer **28** both include polyvinyl chloride. In alternative embodiments, the backing layer **28** can be formed from an elastic material, such as flexible polyether or polyaliphatic urethanes or fabrics with built in elastic fibers, which can be formed from urethane or rubber materials. Backing layer **24** can have a thickness in the range of between about 0.005 and 0.02 inches (0.12 and 0.51 mm).

In accordance with the invention, a plurality of apertures 30 are formed in retroreflective sheeting 10 and extend through the thickness of retroreflective structure 10. The apertures are of sufficient size and spacing from one another to allow the average person to see through the otherwise opaque structure. The apertures 30 can be formed, such as by punching holes in the structure using a suitable tool of various shapes including circles, ovals, rectangles, squares, etc. Also, the apertures can be in the shape of letters or a logo. Apertures 30 can be uniformly or randomly arranged in an array on the structure. Typically, the apertures 30 can be circles having a diameter in the range of between about 0.25 and 0.75 inches (6.35 and 19.05 mm). The array of apertures can cover about 50 percent of the surface area of the retroreflective structure. The apertures provide breathability to the structure. The retroreflective structure, when superimposed over another perforated structure, can result in a moiré effect. Such configurations can be incorporated into clothing or footwear to provide a decorative pattern while providing retroreflectivity for safety.

The base film and prism array portion of one embodiment of the retroreflective structure 10 can be formed by one of the methods disclosed in U.S. Pat. No. 3,684,348, issued to Rowland on Aug. 15, 1972; U.S. Pat. No. 3,689,346, issued to Rowland on Sep. 5, 1972; U.S. Pat. No. 3,811,983, issued to Rowland on May 21, 1974; U.S. Pat. No. 3,830,682, issued to Rowland on Aug. 20, 1974; U.S. Pat. No. 3,975,083, issued to Rowland on Aug. 17, 1976; U.S. Pat. No. 4,332,847, issued to Rowland on Jun. 1, 1982; U.S. Pat. No. 4,801,193, issued to Martin on Jan. 31, 1989; U.S. Pat. No. 5,229,882, issued to Rowland on Jul. 20, 1993; U.S. Pat. No. 5,236,751, issued to Martin et al. on Aug. 17, 1993; U.S. Pat. No. 5,264,063, issued to Martin on Nov. 23, 1992; U.S. Pat. No. 5,376,431, issued to Rowland on Dec. 27, 1994; U.S. Pat. No. 5,491,586, issued to Phillips on Feb. 13, 1996; U.S. Pat. No. 5,512,219, issued to Rowland on Apr. 30, 1996; U.S. Pat. No. 5,558,740, issued to Bernard et al. on Sep. 24, 1996; U.S. Pat. No. 5,592,330, issued to Bernard on Jan. 7, 1997; and U.S. Pat. No. 5,637,173, issued to Martin et al. on Jun. 10, 1997. The teachings of each patent are incorporated herein by reference.

In one embodiment, a six mil (0.15 mm) polyvinyl chloride film is laminated to a two mil (0.05 mm) polyethylene terepthalate (PET) carrier. The polyvinyl chloride film is tie coated and retroreflective prisms are cast on the tie coated polyvinyl chloride film. The retroreflective prisms are metalized. The metalized layer may or may not need to be protected by a coating of some type depending on the application requirements. In embodiments where a silver appearance of metalization is not preferred, a color (either the same color as the top surface or another) can be printed or coated on the metalized layer. A top view of the retroreflective structure is shown in FIG. 2.

Referring now to FIG. 4, a preferred method of forming the invention will now be described in further detail. A metalized retroreflective structure film 100, formed as described above, is unwound from roll 102 and directed to a device 104, such as a step and repeat die punch system, for punching apertures in retroreflective structure film 100. The metalized retroreflective structure film 100 is wound up at windup station 106. The punched particles 50 of retroreflective film described in detail above and shown in FIG. 3 drop onto auto platen 105 and are collected from platen 105. Alternatively, as shown in FIG. 4, the particles 50 can be directly applied from device 104 to an adhesive coated substrate 110, such as a fabric, which is unwound from fabric roll 112, as shown in FIG. 4. Particles 50 can also be

dispersed onto the adhesive side 113 of the adhesive coated substrate 110 from particle dispenser 114. Pinch rollers 116 press the particles against adhesive coated substrate 110. Any loose particles are caught in tray 118 as the adhesive coated substrate and particles exit pinch rollers 116. Top film 122 is unrolled from top film roller 124 and is laminated to adhesive coated substrate with particles in between the two layers by laminating rollers 126. The laminated structure 127 is wound up on windup roller 128.

The particles are suitable for use as decorative or conspicuity particles on clothing, T-shirt signs, pavement marking lines, traffic signs, bicycle helmets, tarpaulins, etc. The particles can be mixed in a gel and applied to a substrate.

For use in low temperature processes (below the melting temperature of PET or polyvinyl chloride), the particles stay intact within the plastic substrate during lamination. For use where the polymer processing temperature exceeds the melting point of PET, the film deforms but the thermoset prisms and/or reflective coating remains intact.

In another embodiment, the perforated retroreflective structure can be applied to the inside of a window. Shown in FIG. 5, polyvinyl film 140 is laminated to a carrier film 142, and the polyvinyl film 140 is coated with tie coat 144. Prisms 146 are cast on the tie coat 144 and the prisms are silver metalized. The structure is perforated with a stamping device to form aperture 150. A barrier film 152, such as paper or polypropylene, is added to the metalized side 148 with an adhesive 151 to provide dimensional stiffness and allows the film to be ink jet printed. Shown in FIG. 6, the carrier film is removed and the polyvinyl film is either screen printed or ink jet printed using plasticol inks 154. By using such inks, the surface of the polyvinyl film 140 has a static cling property, thereby allowing the structure to be applied on the inside of a window 156. Screen printing is a preferred embodiment for long runs or ultraviolet light resistant applications. In another embodiment, a PET film can be used for the top layer for printing on. In yet another embodiment, a dye receptive film can be formed on or attached to the polyvinyl film 140 for reception of inks and the like.

The perforated retroreflective structure can be applied to the outside of a window. Shown in FIG. 7, a method for forming the structure includes applying a tie coat 160 to PET film 162. Prisms 164 are cast on the tie coat 160 and then metalized to form metalized layer 166. The metalized prisms are coated with a removable acrylic-based adhesive 168, preferably with a black pigment incorporated therein, and a silicone coated paper release liner is applied to the acrylic-based adhesive. The film is perforated with a perforator to form aperture 172. A barrier film 174, such as paper or polypropylene, is attached to the release liner 170 to provide additional dimensional stiffness. The film can then be printed on the exposed PET side with screening 176, ink jet printing or another suitable method. Ink jet printers can be a pigmented solvent system that can offer ultraviolet light resistance for about twelve months. As shown in FIG. 8, the temporary release liner 170 is removed and the retroreflective structure can be attached to the outside of a window 180.

In another embodiment, shown in FIG. 9, a polyvinyl film can be laminated to a carrier film, such as a two mil (0.05 mm) PET film 162, and then the polyvinyl film 182 is tie coated. Retroreflective prism elements are cast on the tie coat 160 and then are metalized. The metalized prisms are coated and the carrier film is printed on by a similar step as discussed in the prior paragraph. The structure can be applied to the outside of a window.

A transflector material for use in airport signs is typically back lit, but it needs to be retroreflective in the event of a

power outage. In one embodiment, the transflector material, shown in FIG. 10, is formed by laminating a polyvinyl film **200** to a carrier film **202**, such as PET, and the polyvinyl film is coated with a tie coat **206**. Prisms **208** are cast on the tie coat **206**. The prisms **208** are metalized with metal layer **210**. The film is perforated to form apertures **212**. The perforated film is laminated to a white diffuse film **214**. Shown in FIG. **11**, the carrier film is then removed from the vinyl film. A transparent adhesive **216** is applied to the polyvinyl film, and the film is applied to a silk screen-type printed sheet **218** of transparent material for use in a sign. The printed sheet **218** can be formed from polyvinyl chloride, polymethyl methacrylate (PMMA), or other suitable materials. A coating can be provided over the printed sheet **218** for purposes such as preventing abrasions to the printed sheet.

A seamless graphic film **220**, as shown in FIG. 12, can be formed to hide or remove seam lines created by a mold. The seam lines **222** are removed by cutting out as much of the seam lines as possible and replacing them with glass beads **224**. A polyvinyl prismatic internal reflective element film **226** with prisms **228** laminated with a PET carrier film **232** is perforated to form apertures **234**. The PET carrier film **232** is removed from the perforated vinyl prismatic film **226**. The perforated retroreflective prismatic film **226** is coated with a light tack removable adhesive so that the reflective surface (window surface) is in contact with the adhesive. Beads **224**, preferably high refractive index glass beads, are coated on the film **220**. In FIG. **13**, the beads **224** attach where the beads are exposed to the adhesive **236** in the apertures **234** of the vinyl prismatic film **220**. The facets of the prisms **228** and the attached beads are metalized with metalized layer **230**. In another embodiment, metalized one or two sided corner cube chips or particles may be bonded to the exposed adhesive to provide additional retroreflective area, glitter effects, and/or color effects. The particles can also include metalized "open-face" cube-corner prisms, such as taught in U.S. application No. 09/488,129, filed Jan. 20, 2000, the teachings of which are incorporated herein by reference. The corner cubes may be of a different size than the corner cubes formed on the film **226**.

As shown in FIG. **14**, base adhesive **238**, preferably a white adhesive, and a backing film **240** are applied to the metalized layer **230**. The low-tack adhesive **236** is removed and the film is coated with a flexible transparent weatherable ink receptive system **242**. The formed structure provides a balanced set of properties with good narrow observation for long distance sight detection and with good angularity for viewing at short distances.

In another embodiment, as shown in FIG. **15**, a flexible film having prisms **252** cast on a tie coat **253** and metalized layer **254** on the facets of the prisms is perforated to form apertures **256**. The perforated film is laminated using an adhesive **257** to a fabric backed material **258**. The film is then extrusion coated with a clear abrasion and ultraviolet light resistant material **260**, such as polyvinyl chloride or polyurethane. In another embodiment, prior to lamination, colored PET glitter pieces **262** are coated onto the surface of perforated film which attaches to the areas where the adhesive is present in the perforations to provide a partially glitter-coated perforated reflective film.

Often white ultraviolet curable ink, either on the facets of the prisms or in the tie coat on the window side of the prisms, is used to achieve the necessary Cap Y to meet industry whiteness specifications. While the white printing enhances the Cap Y performance, it also destroys the retroreflectivity of the prisms it covers, thereby effectively destroying sometimes about thirty percent of the retroreflectivity. The white printing can be in the form of a logo, lettering, etc. In addition, the step of printing can expose the prismatic film to excessive heat which can negatively impact the resulting retroreflectivity. Further, printing on the tie coat reduces the run speeds because of the difficulty in curing the prisms.

FIG. **16** illustrates another embodiment of a retroreflective structure **10'** in accordance with the invention. This embodiment is similar to the embodiment of FIG. 1 but further includes a second prism array **14'**, which is formed on the base film **12'**, attached to a second side of the layer **28**. Thus, light rays R are retroreflected from both sides of the structure **10'**. As in other embodiments, a plurality of apertures **30** are formed in the retroreflective sheeting **10'**. The punched particles **51'** from apertures **30**, as shown in FIG. **17**, can be used for decorative or conspicuity purposes.

FIG. **18** illustrate another embodiment of a retroreflective structure which includes a second base film **12'** having a prism array **14'**. This arrangement provides additional retroreflectivity in the aperture **30** area. The prism array **14'** can further include a reflective coating deposited on the surface of the dihedral facets **20'**. Further, backing layer **28** can be attached to the prism area **14'**. FIG. **19** is similar to FIG. **18** and further includes backing layer **28** disposed between the prism arrays **14** and **14'**.

FIG. **20** illustrates a further embodiment of a retroreflective structure in which the prism array **14'** and base film **12'** as disposed on the top side of the film. In one embodiment, the prism array **14'** is bonded to the base film **12** by a substantially clear adhesive **15**. The prisms suspended over the apertures **30** are air-backed and provide retroreflection at the apertures. The remaining prisms are "wetted-out" by the adhesive **15** and do not provide retroreflection.

EQUIVALENTS

While this invention has been particularly shown and described with references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. Those skilled in the art will recognize or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described specifically herein. Such equivalents are intended to be encompassed in the scope of the claims.

What is claimed is:

1. A retroreflective structure comprising:

a) a film having a first side and a second side;

b) a first array of retroreflective cube-corner elements attached to the first side of the film; and

c) an array of apertures through the retroreflective structure within the array of retroreflective cube-corner elements, the apertures formed by removing a portion of the film and the elements.

2. The retroreflective structure of claim 1 further comprising a second array of retroreflective cube-corner elements attached to the second side of the film.

3. The retroreflective structure of claim 2 wherein the retroreflective cube-corner elements of the first array and the second array of retroreflective cube-corner elements include a metalized reflective layer.

4. The retroreflective structure of claim 1 wherein both sides of the film retroreflect incoming light.

5. The retroreflective structure of claim 2 further comprising a first polymer layer attached to the first array of

retroreflective cube-corner elements and a second polymer layer attached to the second array of retroreflective cube-corner prisms.

6. The retroreflective structure of claim 5 wherein the first polymer layer and the second polymer layer include a transparent polymer.

7. The retroreflective structure of claim 1 further comprising a polymer layer attached to the first array of retroreflective cube-corner elements and a barrier film covering at least some of the apertures for providing stiffness to the retroreflective structure while an ink or paint is applied to the polymer layer.

8. The retroreflective structure of claim 1 wherein the retroreflective structure is attached to a window.

9. The retroreflective structure of claim 8 further comprising an adhesive disposed between the cube-corner elements and an outer surface of the window.

10. The retroreflective structure of claim 1 further comprising a polyvinyl film attached to the first array of retroreflective cube-corner elements and further comprising a carrier film disposed on the polyvinyl film opposite the cube-corner elements.

11. The retroreflective structure of claim 10 further comprising an ink or paint applied to the carrier film.

12. The retroreflective structure of claim 11 wherein the retroreflective structure is applied to an outer surface of a window.

13. The retroreflective structure of claim 1 further comprising a polymer layer attached to the first array of retroreflective cube-corner elements, wherein an ink or paint applied to the polymer layer.

14. The retroreflective structure of claim 13 wherein the retroreflective structure is attached to an inner surface of a window.

15. A retroreflective particle comprising:

a) a film having a first side and a second side;

b) a first array of retroreflective cube-corner elements attached to the first side of the film; and

c) a second array of retroreflective cube-corner elements attached to the second side of the film.

16. The retroreflective particle of claim 15 wherein a plurality of the retroreflective particles are attached to an adhesive coated substrate.

17. The retroreflective particle of claim 16 wherein a top film is laminated over the retroreflective particles on the adhesive coated substrate.

18. The retroreflective particle of claim 15, wherein the retroreflective particles are mixed with a gel.

19. A method for forming a retroreflective structure, comprising:

a) providing a film having a first side and a second side;

b) attaching a first array of retroreflective cube-corner elements to the first side of the film; and

c) perforating the array of retroreflective cube-corner elements and the film to remove a portion of the retroreflective cube-corner elements and the film to form an array of apertures through the retroreflective structure.

20. The method of claim 19 further comprising the step of attaching a second array of retroreflective cube-corner elements to the second side of the film.

21. The method of claim 19 wherein the array of retroreflective cube-corner elements is made retroreflective by applying a metalized reflective layer to the array of prismatic elements.

22. The method of claim 19 further including the step of:

d) collecting retroreflective particles formed by perforating the array of retroreflective elements and the film.

23. A transflector comprising:

a) a film;

b) an array of retroreflective cube-corner elements attached to a first side of the film;

c) an array of apertures through the retroreflective structure within the array of retroreflective cube-corner elements, the apertures formed by removing a portion of the film and the elements; and

d) a printed sheet attached to a second side of the film.

24. The transflector of claim 23 wherein the retroreflective cube-corner elements include a metalized reflective layer.

25. The transflector of claim 23 wherein a diffuse film is attached to the metalized reflective layer.

26. A retroreflective structure comprising:

a) a film;

b) an array of retroreflective cube-corner elements attached to the film;

c) an array of apertures through the retroreflective structure within the array of retroreflective cube-corner elements; and

d) a plurality of beads within the array of apertures.

27. The retroreflective structure of claim 26 further comprising an ink receptive system disposed on the film.

28. The retroreflective structure of claim 26 wherein the retroreflective cube-corner elements include a metalized reflective layer.

29. The retroreflective structure of claim 26 wherein the apertures are formed by removing a portion of the film and the elements.

30. A retroreflective structure comprising:

a) a film having a first side and a second side;

b) an array of retroreflective cube-corner elements attached to the first side of the film;

c) an array of apertures through the retroreflective structure within the array of retroreflective cube-corner elements, the apertures formed by removing a portion of the film and the elements; and

d) an ultraviolet light resistant layer disposed on the second side of the film.

31. The retroreflective structure of claim 30 further comprising colored polyethylene terepthalate pieces disposed between the second side of the film and the ultraviolet light resistant layer.

32. The retroreflective structure of claim 31 wherein the retroreflective cube-corner elements include a metalized reflective layer.

33. A retroreflective structure comprising:

a) a film;

b) an array of retroreflective cube-corner elements attached to the film;

c) an array of apertures through the retroreflective structure within the array of retroreflective cube-corner elements; and

d) a plurality of retroreflective particles within the array of apertures.

34. The retroreflective structure of claim 33 wherein the retroreflective particles include a film having a first side and a second side and a first array of retroreflective cube-corner elements attached to the first side of the film.

35. The retroreflective structure of claim 34 wherein the retroreflective particles further include a second array of

retroreflective cube-corner elements attached to the second side of the film.

36. A retroreflective structure comprising:

a) a first film having a first side and a second side;

b) a first array of retroreflective cube-corner elements attached to the first side of the first film;

c) an array of apertures through the retroreflective structure within the first array of retroreflective cube-corner elements;

d) a second film having a first side and a second side, the second side being disposed adjacent to the first array of retroreflective cube-corner elements; and

e) a second array of retroreflective cube-corner elements attached to the first side of the second film.

37. The retroreflective structure of claim 36 further comprising a backing layer disposed between the first array of retroreflective cube-corner elements and the second array of retroreflective cube-corner elements.

38. The retroreflective structure of claim 36 further comprising a backing layer attached to the second array of retroreflective cube-corner elements.

39. The retroreflective structure of claim 36 wherein the apertures are formed by removing a portion of the film and the elements.

40. The retroreflective structure of claim 36 wherein the second array of retroreflective cube-corner elements is made retroreflective by applying a metalized reflective layer to the elements.

41. A retroreflective structure comprising:

a) a first film having a first side and a second side;

b) a first array of retroreflective cube-corner elements attached to the first side of the first film;

c) an array of apertures through the retroreflective structure within the first array of retroreflective cube-corner elements;

d) a second film having a first side and a second side; and

e) a second array of retroreflective cube-corner elements attached to the first side of the second film, the second array of retroreflective cube-corner elements being attached to the second side of the first film.

42. The retroreflective structure of claim 41 further comprising a backing layer attached to the first array of retroreflective cube-corner elements.

43. The retroreflective structure of claim 41 wherein at least some of the cube-corner elements of the second array cover the at least some of the apertures such that the at least some of the cube-corner elements are air-backed.

44. The retroreflective structure of claim 41 wherein the second array of retroreflective cube-corner elements is attached to the second side of the first film by a substantially clear adhesive.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 6,481,857 B2
DATED : November 19, 2002
INVENTOR(S) : Peter R. Smith

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 10,
Lines 9 and 10, delete the word "retroreflective stucture" and substitute therefor the word -- film --.

Column 12,
Line 20, delete the second and third ocurrences of the word "the".

Signed and Sealed this

Twenty-second Day of April, 2003

JAMES E. ROGAN
Director of the United States Patent and Trademark Office

US006323266B2

(12) **United States Patent**
Phillips

(10) **Patent No.:** **US 6,323,266 B2**
(45) **Date of Patent:** ***Nov. 27, 2001**

(54) **EXTENDED LIFE FLUORESCENCE POLYVINYL CHLORIDE SHEETING**

(75) Inventor: **Edward D. Phillips**, Oakville, CT (US)

(73) Assignee: **Reflexite Corporation**, Avon, CT (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **09/756,430**

(22) Filed: **Jan. 8, 2001**

Related U.S. Application Data

(63) Continuation of application No. 09/233,965, filed on Jan. 20, 1999, now Pat. No. 6,191,200.

(60) Provisional application No. 60/072,026, filed on Jan. 21, 1998.

(51) **Int. Cl.**[7] **C08K 5/07**; C09B 1/00; B32B 15/08

(52) **U.S. Cl.** **524/91**; 524/359; 8/508; 8/675; 428/424.6; 428/463; 428/500; 428/515; 428/691

(58) **Field of Search** 524/102, 91, 359; 428/412, 424.6, 463, 500, 515, 691; 8/508, 675

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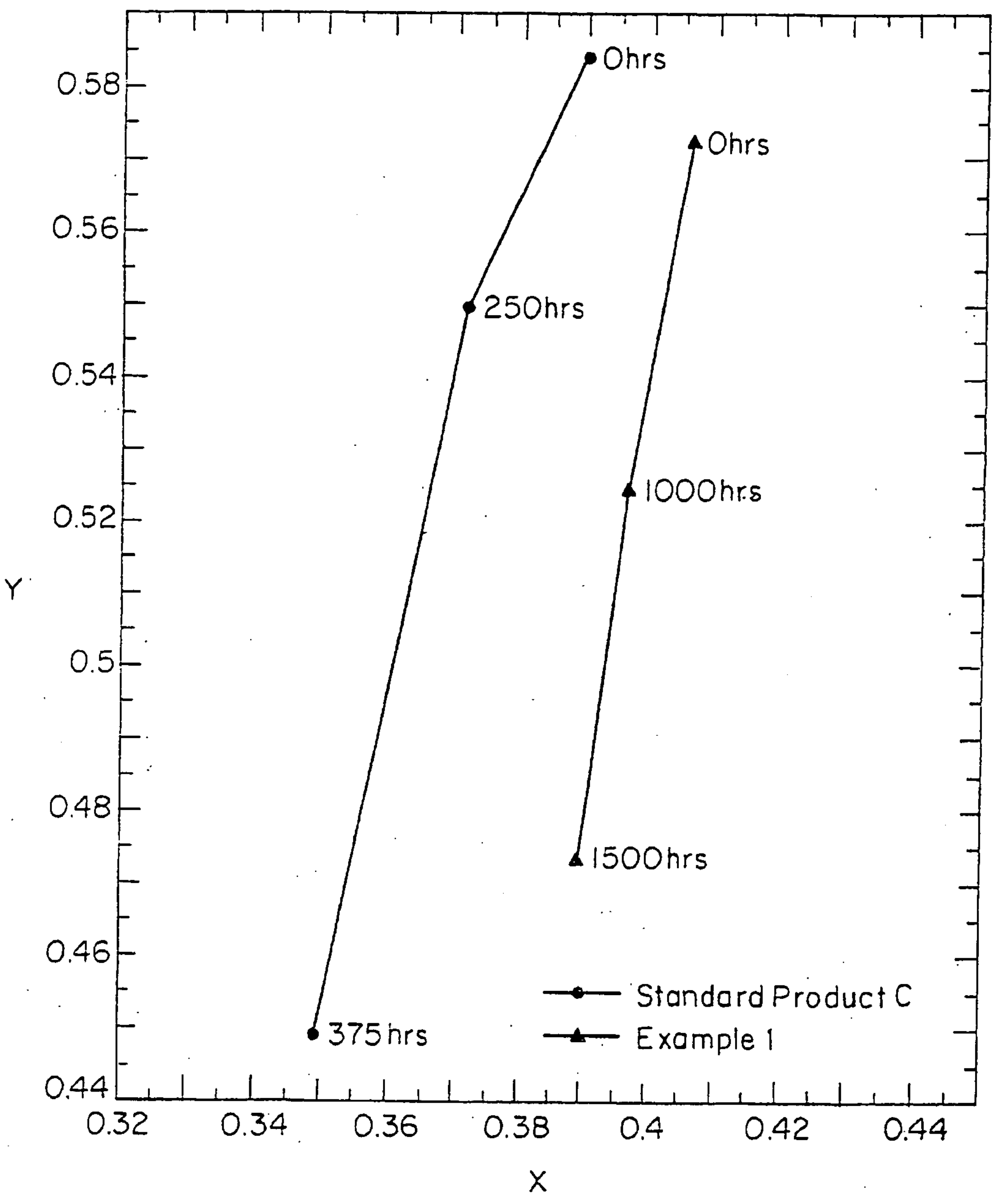
(57) **ABSTRACT**

An extended life fluorescent polyvinyl chloride sheeting and a method for forming the sheeting are disclosed. The sheeting includes a polyvinyl chloride film having a fluorescent colorant incorporated therein. A protective polymer layer is attached to the polyvinyl chloride film. A light filtering agent is incorporated into the protective layer, wherein the filter agent blocks the 425 nm and lower wavelengths of the visible spectrum.

26 Claims, 3 Drawing Sheets


0hrs
0hrs
250hrs
1000hrs
1500hrs
375hrs
Standard Product C
Example 1
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0.52
0.5
0.48
0.46
0.44
Y
0.32
0.34
0.36
0.38
0.4
0.42
0.44
X

FIG. 1

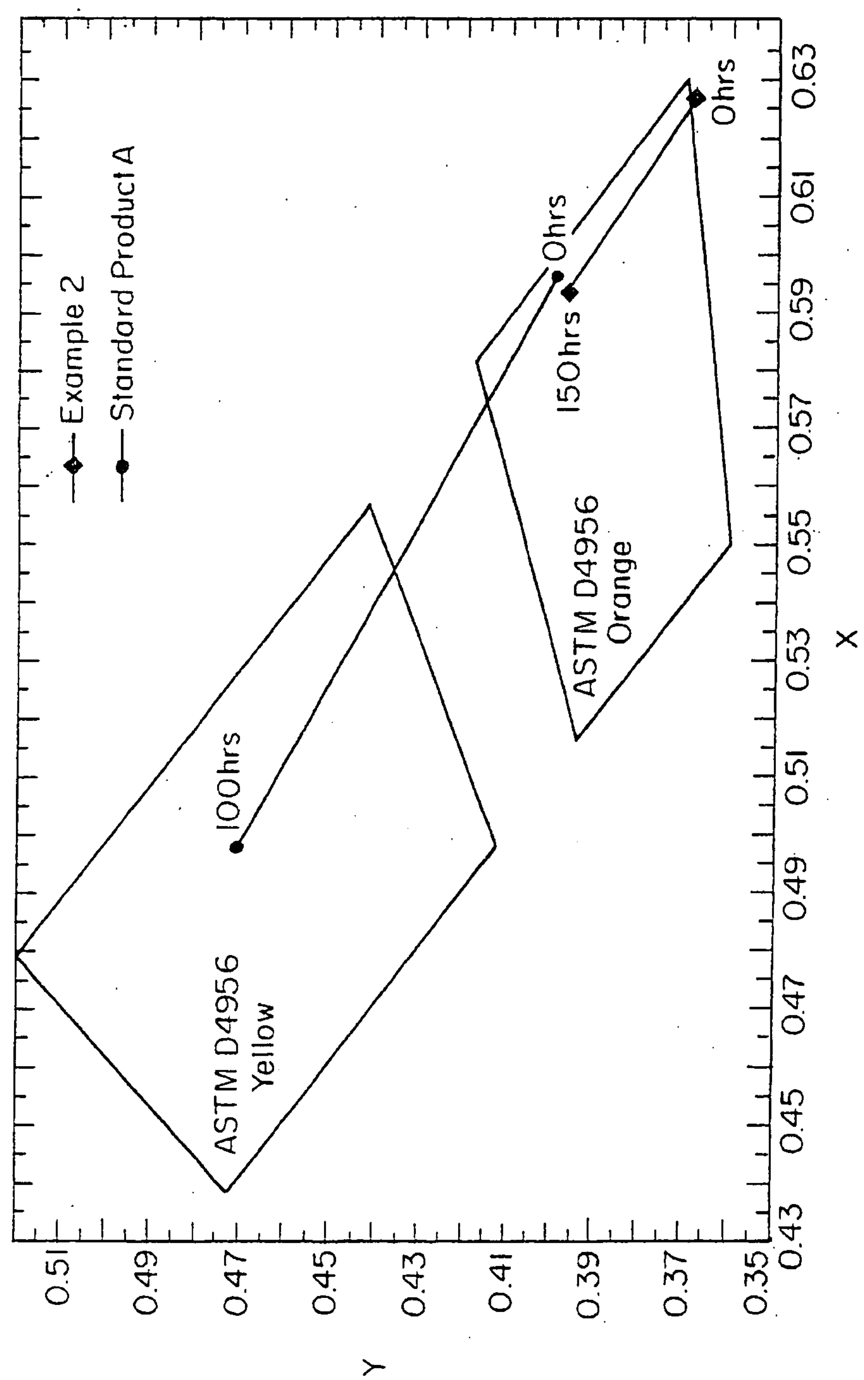
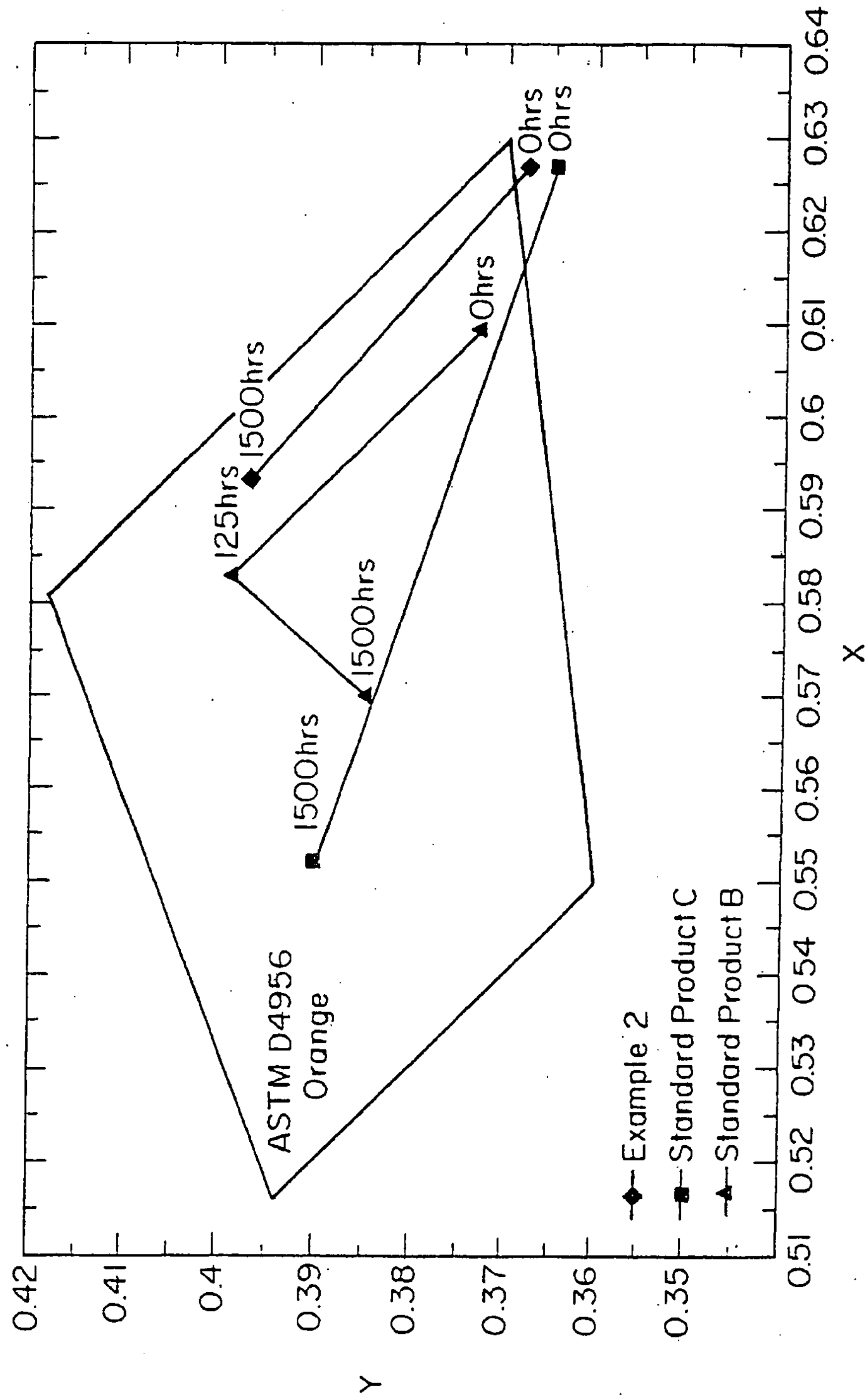

Example 2
Standard Product A
0hrs
0hrs
150hrs
100hrs
ASTM D4956
Orange
ASTM D4956
Yellow
X
Y
0.43
0.45
0.47
0.49
0.51
0.53
0.55
0.57
0.59
0.61
0.63
0.35
0.37
0.39
0.41
0.43
0.45
0.47
0.49
0.51

FIG. 2



0.42
0.41
0.4
0.39
0.38
0.37
0.36
0.35
Y
0.51
0.52
0.53
0.54
0.55
0.56
0.57
0.58
0.59
0.6
0.61
0.62
0.63
0.64
X
ASTM D4956
Orange
0hrs
0hrs
0hrs
1500hrs
125hrs
1500hrs
1500hrs
Example 2
Standard Product C
Standard Product B

FIG. 3

EXTENDED LIFE FLUORESCENCE POLYVINYL CHLORIDE SHEETING

RELATED APPLICATION

This present application claims the benefit of U.S. Provisional Patent Application No. 60/072,026, filed on Jan. 21, 1998. This application is a continuation of application Ser. No. 09/233,965, filed on Jan. 20, 1999 now U.S. Pat. No. 6,191,200. The entire teachings of each application are incorporated herein by reference.

BACKGROUND OF THE INVENTION

The advantages of the high visibility of fluorescent materials is well known. However, poor color fastness in the presence of sunlight has made their use in some applications limited to short-lived, temporary applications. These applications include roadside work zone signs, vehicle conspicuity signs, etc.

Plasticized polyvinyl chloride has been used extensively for retroreflective sheeting applications. In roadside work zone applications, flexible, roll-up signage formed of polyvinyl chloride provides an improved safety upon impact by a vehicle over rigid signage. However, the fluorescent colored polyvinyl chloride signs can fade to a clear film quickly after exposure to sunlight as the fluorescent colorant is consumed with lengthy exposure to ultraviolet light emitted by the sun. However, the retroreflective prism structure continues to function.

Some polymers, such as polycarbonate, that have a fluorescent colorant include a hindered amine light stabilizer compound.

SUMMARY OF THE INVENTION

The present invention includes an extended life fluorescent polyvinyl chloride sheeting and a method for forming the sheeting.

The sheeting includes a polyvinyl chloride film having a fluorescent colorant incorporated therein. A protective polymer layer is attached to the polyvinyl chloride film. A light filtering agent is incorporated into the protective polymer layer, wherein the filter agent blocks the 425 nm and lower wavelengths of the visible spectrum.

The method includes providing a polyvinyl chloride film having a fluorescent colorant incorporated therein. A protective polymer layer is attached to the polyvinyl chloride film. The protective polymer layer includes a light filtering agent that blocks the 425 nm and lower wavelengths of the visible spectrum, thereby forming the extended life fluorescent polyvinyl chloride sheeting.

The present invention has an advantage of providing fluorescent protection to a polyvinyl chloride sheeting while providing solvent resistance, printability, low coefficient of friction and can incorporate water shedding properties, such as hydrophobic and hydrophilic additives where desirable.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a chart of the results of an accelerated weathering color test of a first sample of the present invention and a first standard product.

FIG. 2 is a chart of the results of an accelerated weathering color test of a second sample of the present invention and a second standard product.

FIG. 3 is a chart of the results of an accelerated weathering color test of the second sample of the present invention and second and third standard products.

DETAILED DESCRIPTION OF THE INVENTION

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention. All percentages and parts are by weight unless otherwise indicated.

Retroreflective materials are typically formed of a sheet of thermoplastic, which has a colorant mixed therein with the polymers. Attached to the sheet of thermoplastic is an array of cube-corner or prismatic retroreflectors as described in U.S. Pat. No. 3,712,706, issued to Stamm on Jan. 23, 1973, the teachings of which are incorporated herein in their entirety by reference. Generally, the prisms are made by forming a master die on a flat surface of a metal plate or other suitable material. To form the cube-corner, three series of parallel equidistant intersecting V-shaped grooves 60 degrees apart are inscribed in the plate. The die is then used to process the desired cube-corner array into a flat plastic surface. When the groove angle is 70 degrees, 31 minutes, 43.6 seconds, the angle formed by the intersection of two cube faces (dihedral angle) is 90 degrees and the incident light is retroreflected back to the source.

The efficiency of a retroreflective structure is the measure of the amount of incident light returned within a cone diverging from the axis of retroreflection. A distortion of the prismatic structure adversely affects the efficiency. Furthermore, cube-corner retroreflective elements have low angularity at some orientation angles, for instance, the elements will only brightly reflect light that impinges on it within a narrow angular range centering approximately on its optical axis. Low angularity arises from the inherent nature of these elements which are trihedral structures having three mutually perpendicular lateral faces. The elements are arranged so that the light to be retroreflected impinges into the internal space defined by the faces, and the retroreflection of the impinging light occurs by internal retroreflection of the light from face to face of the element. Impinging light that is inclined substantially away from the optical axis of the element (which is a trisection of the internal space defined by the faces of the element) strikes the face at an angle less than its critical angle, thereby passing through the face rather than being reflected. Further details concerning the structures and the operation of cube-corner microprisms can be found in U.S. Pat. No. 3,684,348, issued to Rowland on Aug. 15, 1972, the teachings of which are incorporated by reference herein in their entirety. The disclosed method is for forming cube-corner microprisms in a cooperatively configured mold. The prisms are bonded to sheeting which is applied thereover to provide a composite structure in which cube-corner microprisms project from one surface of the sheeting.

The array of retroreflectors includes optical elements that are known in the art, such as cube-corner prisms, four-sided prisms, Fresnel lenses, rounded lenses, etc. In one embodiment, the array of retroreflectors has a window side and a facet side. The array of retroreflectors are formed of a transparent flexible polymer polyvinyl chloride. Preferably, the polymer is cast in a mold with a monomer or oligomer, and the polymerization is initiated by ultraviolet radiation. Preferably, the array of retroreflectors is formed of cube-corner prism elements having a length along each cube side edge in the range of between about 0.003 and 0.02 inches (0.076 and 0.51 mm). In a preferred embodiment, the prism elements have a length along each cube-side edge in the range of between 0.0049 and 0.02 inches (0.124 and 0.51

mm). In a particularly preferred embodiment, each cube-side edge has a length of about 0.0049 inches (0.124 mm).

An adhesive can be applied to the prism facets for attaching a backing layer to the retroreflective structure. If an adhesive is employed on the prism facets, the adhesive can cause the surface of the prisms to wet, thereby destroying the air interface and eliminating the ability of the prism to retroreflect. As a result, the reflective coating is preferably deposited on the surface of the dihedral facets. Typically, the reflective coating is formed by sputtering aluminum, silver or gold or by vacuum metalization. Alternatively, metal lacquers, dielectric coatings and other specular coating materials can be employed.

The retroreflective structure **24** can be formed by numerous methods. Some of the methods for forming a retroreflective structure are disclosed in U.S. Pat. No. 3,684,348, issued to Rowland on Aug. 15, 1972; U.S. Pat. No. 3,689,346, issued to Rowland on Sep. 5, 1972; U.S. Pat. No. 3,811,983, issued to Rowland on May 21, 1974; U.S. Pat. No. 3,830,682, issued to Rowland on Aug. 20, 1974; U.S. Pat. No. 3,975,083, issued to Rowland on Aug. 17, 1976; U.S. Pat. No. 4,332,847, issued to Rowland on Jun. 1, 1982; U.S. Pat. No. 4,801,193, issued to Martin on Jan. 31, 1989; U.S. Pat. No. 5,229,882, issued to Rowland on Jul. 20, 1993; U.S. Pat. No. 5,236,751, issued to Martin et al. on Aug. 17, 1993; U.S. Pat. No. 5,264,063, issued to Martin on Nov. 23, 1992; U.S. Pat. No. 5,376,431, issued to Rowland on Dec. 27, 1994; U.S. Pat. No. 5,491,586, issued to Phillips on Feb. 13, 1996; U.S. Pat. No. 5,512,219, issued to Rowland on Apr. 30, 1996; U.S. Pat. No. 5,558,740, issued to Bernard et al. on Sep. 24, 1996; U.S. Pat. No. 5,592,330, issued to Bernard on Jan. 7, 1997; and U.S. Pat. No. 5,637,173, issued to Martin et al. on Jun. 10, 1997. The teachings of each patent are incorporated herein by reference.

The advantages of the high visibility of fluorescent materials is well known, but their poor color fastness in the presence of ultraviolet light has made their use in some important applications, such as roadside work zone, vehicle conspicuity, etc., limited to short-lived, temporary applications.

Plasticized vinyl has been used extensively for retroreflective sheeting applications. In applications, such as roadside work zones, it has also been well established that flexible so-called "roll-up" signage usually made of highly plasticized polyvinyl chloride provide greatly improved safety upon impact over rigid signage.

The use of a free radical absorber of the hindered amine light stabilizer type, such as 2,2,6,6-tetramethyl piperdine, has been used to improve the color fastness of polycarbonate colored with the thioxanthene, perylene imide, and thioindigold fluorescent colorants (U.S. Pat. No. 5,605,761).

It has been found that by use of a protective polymer layer or coating or film layer made of polyacrylate, polyurethane, or polyurethane acrylates which incorporate ultraviolet absorbers of the benzophenone or benzotriazole-type along with a light filtering agent which blocks out the short wavelengths of the visible spectrum (425 nm and lower) over a highly plasticized flexible fluorescent polyvinyl chloride sheeting containing a suitable hindered amine, color fastness can be greatly improved. The wavelengths of visible light extend between about 400 nm for the extreme violet and about 720 nm for the deep red. The visible light filtering agent should impart color that can obscure the desirable daytime visibility of the fluorescent product. A suitable visible light filtering agent is Color Index Solvent Yellow 93. A suitable amount of filtering agent is in a range of between about 0.05 and 5.0 percent. A preferred range is between about 1.0 and 1.5 percent. A suitable hindered amine for use with polyvinyl chloride is bis-(1,2,2,6,6-tetramethyl-4-piperidinyl) sebacate. A suitable amount of hindered amine is in a range of between about 0.1 and 7.0 percent. A preferred range is between about 0.2 and 1.5 percent.

Through selection of coating ingredients in the top coat protective polymer layer, the fluorescent protection features can be coupled with a wide variety of different performance properties including but not limited to cold temperature flexibility, solvent resistance, printability, low coefficient of friction, and specialized water shedding properties (i.e. hydrophobic, hydrophilic).

The colors of principal interest in the area of fluorescent retroreflective sheeting are lime-yellow and red-orange.

The base material of wavelength filtering layer can be a polymer film, such as polyvinyl chloride, polyacrylate, polyurethane, polyvinylidene chloride, fluoropolymer, or highly stabilized copolymers, such as vinylidene fluoride-hexafluoropropylene. This film can be laminated directly to fluorescent colored layer through heat and pressure in some cases, such as some urethanes, or by use of an adhesive layer. The thickness of the wavelength filtering layer can be in the range of between about 0.1 and 10 mils (0.00254 and 0.254 mm). The base material of the wavelength filtering layer can also be applied to the fluorescent colored layer as a coating. This coating can be solvent borne, water-based, two-part, or radiation curable in nature.

The wavelength filtering layer is protective to the colorant in the fluorescent colored layer by incorporation of ultraviolet light absorbers or selected colorants or both which can block the wavelengths that are destructive to the colorant but still allow the day bright color to be visible. The daytime visibility of the product can be temporarily enhanced by the incorporation of some fluorescent colorant into the wavelength filtering layer, provided that the wavelengths generated by fluorescent colorant in the filtering layer are not destructive to the primary fluorescent colorant in the fluorescent colored layer.

For the fluorescent colored layer, a base polymer of polyvinyl chloride is preferred. Incorporated into this layer is the primary fluorescent colorant of the product. The most commonly used, widely available, and lowest cost fluorescent colorants are the xanthene based fluorescent dyes. This group, which encompasses both the fluorenes and the fluorones, includes such dyes as fluoresceins, rhodamines, eosines, phloxines, uranines, succineins, sacchareins, rosamines, and rhodols. The dyes are noted for their brilliant daytime colors, high intensity color compatible fluorescence, and poor light fastness. Other fluorescent dyes displaying better light fastness include pyranines, anthraquinones, benzopyrans, thioxanthenes and perylene imides.

The prism layer can be compression molded or cast directly onto the fluorescent colored layer or attached by means of a tiecoat. The prism layer can be formed of polyvinyl chloride, an acrylate or other suitable polymer.

This prismatic sheeting configuration can be sealed to any number of backing materials by radio frequency, thermal, or sonic welding methods. The daytime color saturation (chroma) properties of a transparent fluorescent material are increased if backed by a white layer, it is desirable to have the backing be white in color on the surface behind the prisms. Alternatively, the prismatic material can be metalized in an aesthetically appealing pattern and laminated to a white pressure sensitive substrate adhesive. Similarly, a

pattern can be printed onto the film prior to casting, or onto the backs of the prisms after casting, using a white ink to enhance the daytime chroma. However, these methods enhance the daytime fluorescent color at the expense of some of the retroreflective area, because the non-metalized prisms that have their facets covered with adhesive do not maintain a differentiation in refractive index that is sufficiently large for internal reflection to occur.

Both of the latter construction alternatives have the advantage of not having an air gap in the construction behind the prism layer. Elimination of the air gap can help augment the physical durability of the sheeting, because each layer of the product has about 100% of its surface bonded to its adjacent layers.

If a reflective material that is environmentally stable yet whiter than aluminum can be coated onto the prism facets, it can allow a fully metalized product to have an adequate "cap Y" to produce a desired daytime color. Silver, chromium, gold, palladium, and platinum are also possibilities.

The product can conform to the Minnesota Department of Transportation Specification 1710 for Fluorescent Orange Retroreflective Sheeting for Use on Work Zone Traffic Control Devices, the teachings of which are incorporated herein by reference in their entirety. It defines a color box (see Product Testing Requirements and Specification section), reflectance limits (30 minimum new, 20 minimum to 45 maximum for weathered (500 Weatherometer hours)), and a table (B) of Minimum Coefficients of Retroreflection approximate the 1,300 hour color retention in a xenon lamp accelerated weathering device.

A series of test samples was prepared for accelerated weathering testing under ASTM G26. The teachings of ASTM G26 are incorporated herein by reference in their entirety.

EXAMPLE 1

A fluorescent lime (yellow-green) colored microprismatic product was formed having a polyvinyl chloride base film. The polyvinyl chloride base film was highly plasticized using phthalate monomeric plasticizers and a xanthene solvent yellow as a colorant with a benzophenone ultraviolet absorber additive having a thickness of about 250μ thick. The film was further protected with a 7μ thick topcoat based on a flexible urethane acrylate oligomer, and containing a benzotriazole ultraviolet absorber and a hindered amine light stabilizer, and C.I. Solvent Yellow 93. This configuration of polyvinyl chloride and additives absorbed eighty-five percent or more of the light having wavelengths of 450 nm and shorter.

EXAMPLE 2

A fluorescent orange colored microprismatic product was formed having a polyvinyl chloride base film. The 350μ thick polyvinyl chloride base film was highly plasticized using phthalate monomeric plasticizers and colored with a fluorescent orange, thioxanthone colorant, a benzophenone ultraviolet absorber additive, and hindered amine light stabilizer. The film was further protected with a clear, 100μ thick, polyvinyl chloride based top film containing a benzophenone ultraviolet absorber additive.

EXAMPLE 3

A fluorescent orange colored microprismatic standard Product A was formed having a polyvinyl chloride base film. The 250μ thick, polyvinyl chloride base film was highly plasticized using phthalate monomeric plasticizers and a mixture of a xanthene solvent yellow and rhodamine B as colorants.

EXAMPLE 4

A fluorescent orange colored microprismatic standard Product B was formed having a polyvinyl chloride base film. The polyvinyl chloride base film is highly plasticized using phthalate monomeric plasticizers. The film was made from a lamination of two 150μ thick polyvinyl chloride films. The first polyvinyl chloride film included a non-fluorescent but very light stable combination of a transparent diazo yellow and organic red pigments. The second polyvinyl chloride film included the highly fluorescent but comparatively fugitive combination of colorants used in Standard Product A.

EXAMPLE 5

A fluorescent lime (yellow-green) colored microprismatic standard Product C was formed having a polyvinyl chloride base film. The 250μ thick, polyvinyl chloride base film was highly plasticized using phthalate monomeric plasticizers and a xanthene solvent yellow colorant.

All of the aforementioned Examples 1–5 included the same microprismatic array composed of a cross-linked acrylated urethane ester. Each of the prismatic films was sealed by radio frequency welding to a polymeric plasticized, opaque white, textured, polyvinyl chloride backing material for purposes of this accelerated weather testing.

All of the samples were mounted onto an aluminum panel with pressure sensitive adhesive and tested in an Atlas model C35 Xenon Weatherometer in accordance with the ASTM G26 test method for a total of 1,500 hours. The teachings of ASTM G26 are incorporated herein in their entirety. The samples were evaluated periodically throughout the duration of the test for color change using a HunterLab LabScan II, LS-6000 Spectrophotometer.

Minimal movement in color coordinates can show color stability. The orange colorant in a standard product can fade to yellow (out of the color box) after approximately 48 hours in a carbon-arc Weatherometer while the orange colorant in a sample of the present invention can still be in the color box after fifteen hundred hours of exposure. An example of a color box is shown in FIG. 2 as defined by the orange color region boundary (Coordinate 1, x=0.550, y=0.360; Coordinate 2, x=0.630, y=0.370; Coordinate 3, x=0.581, y=0.418; Coordinate 4, x=0.516, y=0.394). The color box coordinates are disclosed in ASTM D4956-95, Table 10 for Color Specification Limits (Daytime) for white, yellow, orange, green, red, blue and brown. The teachings of ASTM D4965-95 are herein incorporated by reference in their entirety. Spectrophotometer or colorimeter having 45°/0° or 0°/45° illumination and viewing geometry is suitable for measuring color. Color coordinates are defined by tristimulus coordinates corresponding to the CIE 1931 Standard Colorimetric System by standard illuminant C.

FIG. 1 shows the degree of color change (distance moved) in CIE 1931 standard color space for Standard Product C (described in Example 5) after 375 hours of testing was greater than the sample described in Example 1 after 1,500 hours of exposure testing. The date point labels indicate hours of exposure in the Weatherometer.

FIG. 2 shows the rapid color change of fluorescent orange Standard Product A (as described in Example 3) after only 100 hours of exposure which resulted in a change in color from orange (0.595, 0.4) to yellow (0.498, 0.47) as compared to the color stability of a sample of the present invention, as described in Example 2, after 1,500 hours of exposure, which maintained its orange color.

FIG. 3 shows the color fastness performance of two commercially available products compared to the present invention as described in Example 2. Standard Product B (Example 4) exhibited rapid color change over the first 125

hours of exposure as the conventional fluorescent colorants faded and then became fairly stable between 125 hours and 1,500 hours when the non-fluorescent pigments are responsible for the color. The Standard Product C (Example 5) also demonstrated a greater over all color change than the embodiment of Example 2. A more significant fact is that the Standard Product C color loss direction indicates a more significant decrease in chroma (shift to the left). This loss of color saturation in the Standard Product C (Example 5) indicates that the embodiment of Example 2 can have better visibility in real world daytime applications.

Equivalents

While this invention has been particularly shown and described with references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. Those skilled in the art will recognize or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described specifically herein. Such equivalents are intended to be encompassed in the scope of the claims.

What is claimed is:

1. An extended life fluorescent polyvinyl chloride sheeting, comprising:

a) a polyvinyl chloride film having a fluorescent colorant and hindered amine light stabilizer incorporated therein; and

b) a protective polymer layer, which is attached to said polyvinyl chloride film, wherein said protective layer includes an ultraviolet absorber.

2. The sheeting of claim 1 wherein said fluorescent colorant includes a xanthene-based fluorescent dye.

3. The sheeting of claim 2 wherein the xanthene-based fluorescent dye includes a dye selected from a group consisting of fluoresceins, rhodamines, eosines, phloxines, uranines, succineins, sacchareins, rosamines, and rhodols.

4. The sheeting of claim 1 fluorescent colorant includes a dye selected from the group consisting of pyranines, anthraquinones, benzopyrans, thioxanthenes and perylene imides.

5. The sheeting of claim 1 wherein the fluorescent colorant includes a dye selected from a group consisting of fluoresceins, rhodamines, eosines, phloxines, uranines, succineins, sacchareins, rosamines, rhodols, pyranines, anthraquinones, benzopyrans, thioxanthenes and perylene imides.

6. The sheeting of claim 5 wherein said protective layer includes a light filtering agent, which is incorporated into said protective layer, said filtering agent blocks the 425 nm and lower wavelengths of the visible spectrum.

7. The sheeting of claim 5 wherein said hindered amine includes bis-(1,2,2,6,6-tetramethyl-4-piperidinyl) sebacate.

8. The sheeting of claim 6 wherein said light filtering agent includes Color Index Solvent Yellow 93.

9. The sheeting of claim 1 wherein said protective polymer layer includes a polymer selected from the group consisting of polyacrylate, polyurethane, polyurethane acrylate, polyvinyl chloride, polyvinyl acetate and polyvinylidene chloride.

10. The sheeting of claim 5 wherein said ultraviolet absorber is selected from the group consisting of benzophenone and benzotriazole.

11. The sheeting of claim 5 wherein said protective polymer layer has a thickness in the range of between about 0.2 mils and about 15 mils.

12. The sheeting of claim 5 wherein said protective polymer layer has a thickness in the range of between about 0.5 mils and about 1.0 mil.

13. The sheeting of claim 5 wherein said polyvinyl chloride film includes a printed pattern.

14. The sheeting of claim 13 wherein said polyvinyl chloride film includes a printed pattern formed of a white ink to enhance daytime chroma.

15. The sheeting of claim 5 wherein the polyvinyl chloride film includes a metalized layer thereon.

16. The sheeting of claim 15 wherein the metalized layer is formed of a metal selected from the group consisting of aluminum, chromium, gold, palladium, platinum and silver.

17. A retroreflective structure formed with the fluorescent polyvinyl chloride sheeting of claim 1.

18. A method for forming an extended life fluorescent polyvinyl chloride sheeting, comprising:

a) providing a polyvinyl chloride film having a fluorescent colorant incorporated therein; and

b) attaching a protective polymer layer to said polyvinyl chloride film, wherein said protective polymer layer includes an ultraviolet absorber.

19. The sheeting of claim 18 wherein the fluorescent colorant includes a dye selected from a group consisting of fluoresceins, rhodamines, eosines, phloxines, uranines, succineins, sacchareins, rosamines, rhodols, pyranines, anthraquinones, benzopyrans, thioxanthenes and perylene imides.

20. The method of claim 19 wherein said protective polymer layer includes a light filtering agent that blocks the 425 nm and lower wavelengths of the visible spectrum, thereby forming the extended life fluorescent polyvinyl chloride sheeting.

21. An extended life fluorescent sheeting, comprising:

a) a polyvinyl chloride film having a fluorescent colorant and hindered amine light stabilizer incorporated therein;

b) a protective polymer layer, which is attached to said polyvinyl chloride film, wherein said protective layer includes an ultraviolet absorber and wherein said protective polymer layer includes a polymer selected from the group consisting of polyacrylate, polyurethane, polyurethane acrylate, polyvinyl acetate and polyvinylidene chloride.

22. The sheeting of claim 21 wherein the fluorescent colorant includes a dye selected from a group consisting of fluoresceins, rhodamines, eosines, phloxines, uranines, succineins, sacchareins, rosamines, rhodols, pyranines, anthraquinones, benzopyrans, thioxanthenes and perylene imides.

23. The extended life fluorescent sheeting of claim 22 wherein said protective layer includes a light filtering agent, which is incorporated into said protective layer, said filtering agent blocks the 425 nm and lower wavelengths of the visible spectrum.

24. The sheeting of claim 22 wherein said ultraviolet absorber is selected from the group consisting of benzophenone and benzotriazole.

25. The sheeting of claim 22 wherein said hindered amine includes bis-(1,2,2,6,6-tetramethyl-4-piperidinyl)sebacate.

26. The sheeting of claim 22 wherein said light filtering agent includes Color Index Solvent Yellow 93.

* * * * *

US005508105A

United States Patent [19]

Orensteen et al.

[11] **Patent Number: 5,508,105**

[45] **Date of Patent: Apr. 16, 1996**

[54] **THERMAL PRINT RECEPTIVE AND FRANGIBLE RETROREFELECTIVE POLYMERIC SHEETINGS**

[75] Inventors: **Bruce D. Orensteen**, St. Paul; **Thomas F. Look**, Ham Lake; **Robert F. Watkins**, Roseville; **Joseph M. McGrath**, Lake Elmo; **Robert V. O'Keefe**, New Brighton; **Joseph R. Zwack**, Roseville, all of Minn.

[73] Assignee: **Minnesota Mining and Manufacturing Company**, St. Paul, Minn.

[21] Appl. No.: **186,751**

[22] Filed: **Feb. 2, 1994**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 33,627, Mar. 16, 1993, abandoned, which is a continuation-in-part of Ser. No. 17,573, Feb. 16, 1993, abandoned.

[51] **Int. Cl.**[6] **B32B 5/16**

[52] **U.S. Cl.** **428/323**; 428/195; 428/325; 428/327; 428/411.1; 428/423.1; 428/424.2; 428/500; 428/522; 428/913

[58] **Field of Search** 428/323, 331, 428/402, 913, 40, 204, 195, 411.1, 325, 327, 423.1, 424.2, 500, 522; 524/493, 847; 359/536

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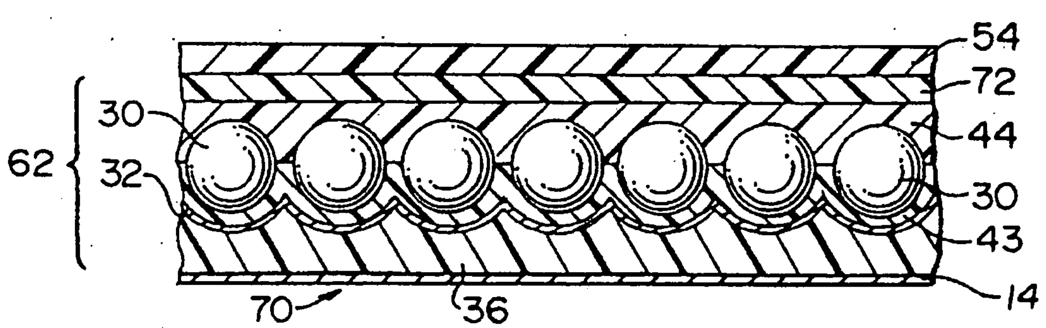
Primary Examiner—Patrick J. Ryan
Assistant Examiner—William A. Krynski
Attorney, Agent, or Firm—Gary L. Griswold; Walter N. Kirn; Robert H. Jordan

[57] **ABSTRACT**

Polymeric sheeting materials directly thermally printed upon with a thermal printing system and a resin-based colorant/binder. The polymeric sheeting materials comprise a core sheet and a thermally print receptive surface on the core sheet. The thermally print receptive surface may be formed from compositions comprising a polyurethane dispersion. The thermally print receptive surface is smooth, transparent, durable, and weatherable.

Signage articles made from the polymeric sheeting materials of the invention may be configured to have the desired combination of frangibility, durability, retroreflectivity and/or low production cost. Frangible, retroreflective signage articles may be produced from the polymeric sheeting materials and may have durable variable information thermally and variably printed directly on the articles.

37 Claims, 3 Drawing Sheets



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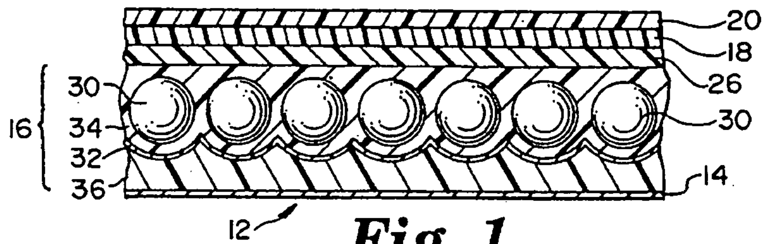

Fig. 1

PRIOR ART

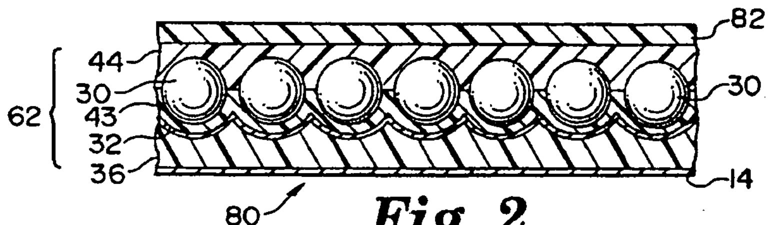

Fig. 2

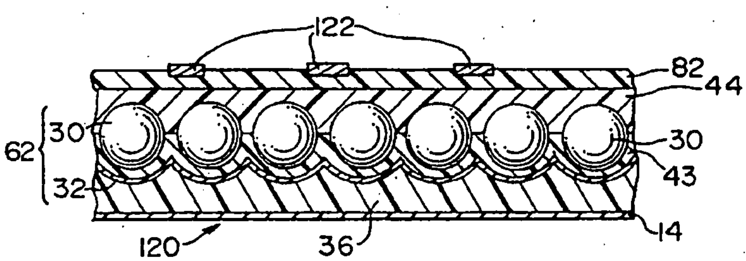

Fig. 3

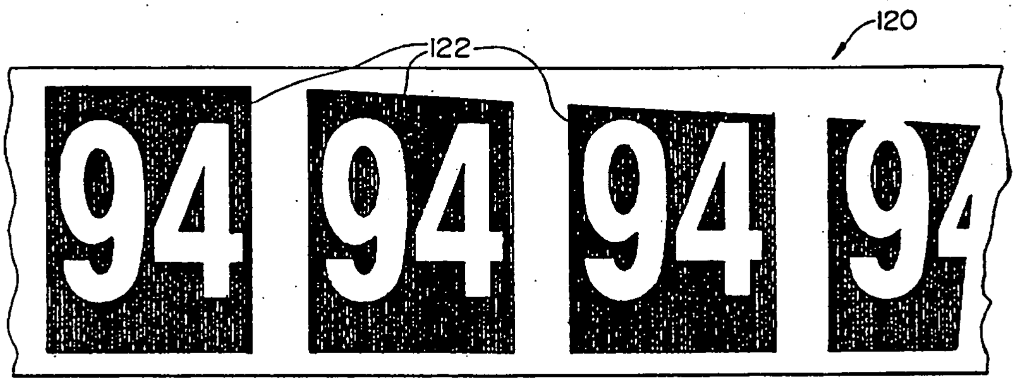

Fig. 4

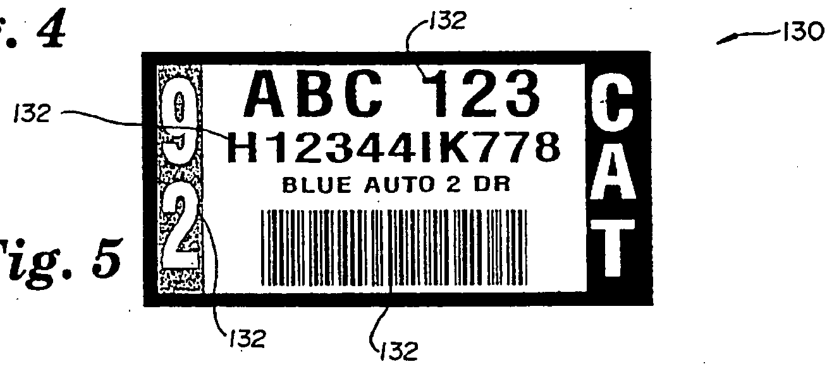

Fig. 5

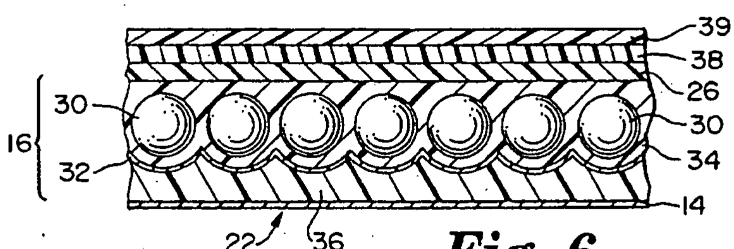

Fig. 6

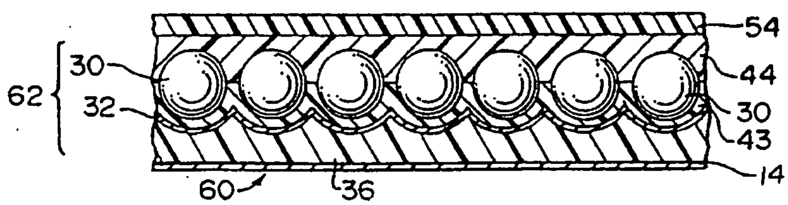

Fig. 7

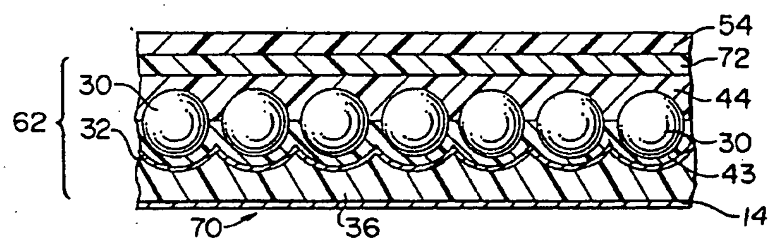

Fig. 8

THERMAL PRINT RECEPTIVE AND FRANGIBLE RETROREFELECTIVE POLYMERIC SHEETINGS

This is a continuation-in-part of U.S. patent application Ser. No. 08/033,627, filed Mar. 16, 1993, which is a continuation-in-part of U.S. patent application Ser. No. 08/017,573, filed Feb. 16, 1993. The disclosures of these applications are incorporated herein by reference.

FIELD OF THE INVENTION

This invention relates to polymeric sheeting materials capable of directly receiving a thermally printed indicia from a resin-based colorant/binder. The invention further relates to sheetings that form frangible, retroreflective, weatherable and/or durable signage articles, comprising multi-function layers that are directly print receptive with resin-based colorant/binder on the upper, exposed surface.

BACKGROUND OF THE INVENTION

Polymeric sheetings have been used in situations where a frangible signage article is desired. Frangible signage articles often are capable of being affixed to a surface, yet are easily damaged or torn when an attempt is made to remove or alter them. Frangibility is generally desired for security reasons, for example, to inhibit fraud, and may be provided to a signage article by thinness, deformability, strong adhesion to the substrate to which an article is affixed, brittleness, and/or ease of separation of various layers of an article.

Polymeric sheetings also have been used to produce signage articles that have retroreflective capabilities. An article possesses a retroreflective capability when it can return a substantial portion of incident light in the direction from which the light originated. Retroreflectivity renders enhanced conspicuity to the article in low or restricted lighting situations, or in situations where sheeting materials must be viewed from a distance.

Polymeric sheetings also have been used to produce signage articles that have good durability. Durability of a signage article may be important in situations where the article may be exposed to harsh vapors, ultraviolet light, temperature or humidity extremes and the like. Abrasion resistance and resistance to cleaning agents and the solvents used in cleaning solutions also are, in some cases, important aspects of durability. If extended useful life is not an important consideration (such as labels for rapid turnover packaging), lower cost non-extended life sheetings may be used.

Polymeric sheetings also have been used to form signage articles having indicia such as alphanumeric characters, bar codes or graphics. Frequently, the signage articles will carry information that is repeated or incrementally varied over a large number of items; for instance, license plate validation stickers may have state or county identifying information repeated on a large number of validation stickers.

Indicia may be printed on the polymeric signage articles by such well known processes as letter press, offset press, screen printing, or hot foil stamping. These types of printing processes normally provide satisfactory print quality, legibility, and adhesion; however, the equipment for these processes can be relatively expensive. In addition, when using letter press and offset press printing, print plates or rubber blankets must be prepared, and when using screen or hot stamp printing, a screen or hot stamp, respectively, must be prepared. The preparation of the plates, blankets, screens,

or stamps can be a costly, time-consuming process. In many cases, a solvent-borne colorant is used, which requires disposing of the solvent in an environmentally-sound manner. Known processes also may necessitate the use of drying ovens and may require a certain amount of drying time. Further, the known means of printing indicia on articles are limited by the ease (or lack thereof) with which the information on individual items can be varied.

The documents discussed below contain disclosures that may be pertinent to the present invention.

U.S. Pat. No. 5,118,930 to Takada discloses a retroreflective sheeting using a polyvinyl chloride topmost layer upon which bar codes may be directly thermally printed.

Commonly-assigned Patent Cooperation Treaty application to Goeb, having international publication number WO 93/12155, discloses label stock having a halogen-free acrylic urethane topmost layer. The application discloses that the additional step of priming the upper surface of the label stock, for example, by corona discharge or with a diluted solution of an acrylate polymer or adhesive, is preferred in order to promote adhesion of inks.

Compositions containing aqueous dispersions of polyurethane and a crosslinker are known to be useful as prime layers between the component layers of multilayer cover films of retroreflective sheetings, or as a prime layer to improve the adhesion of a cover layer to underlying components of the retroreflective sheeting. For instance, commonly-assigned U.S. Pat. No. 4,896,943 to Tolliver et at., discloses encapsulated-lens retroreflective sheetings and the use of a composition containing urethane and crosslinker as a prime layer about 2 microns thick, to improve the adhesion of a cover layer to an underlying binder layer. In addition, commonly-assigned U.S. Pat. No. 5,066,098 to Kult et al., discloses the use of a similar composition as the inner layer of a cover film of an encapsulated-lens retroreflective sheeting.

The above-cited Tolliver patent also discloses the subsequent application of inks to the upper surface of an encapsulated-lens retroreflective sheeting. The Tolliver patent suggests the use of a urethane and aziridine composition to form a conditioning layer on the outside surface of a dual layer cover film of a retroreflective sheeting. However, direct thermal printing is generally difficult on such encapsulated-lens sheetings because of their undulating upper surface. It is known to use a prime layer of a polyurethane about 2 microns thick over an enclosed-lens retroreflective sheeting that has a cover layer such as ethylene/acrylic acid.

U.S. patent application Ser. No. 08/030,672, filed Mar. 12, 1993 by Watkins, et at., (commonly assigned and incorporated herein by reference) discloses compositions comprising an aqueous aliphatic or aromatic polyurethane dispersion and an acrylic emulsion for forming clear coats at least ten microns thick over finished frangible articles having indicia printed thereon. Such clear coats are desired in order to bury or embed the indicia. Watkins, et at., also discusses roll coating of indicia onto embossed, nonfrangible articles having such clear coats.

Commonly-assigned U.S. Pat. No. 4,767,659 to Bailey et at. (incorporated herein by reference) discloses enclosed-lens retroreflective sheetings having a thermoplastic cover film comprised either of aliphatic urethanes, copolymers of ethylene or propylene, or homopolymers of ethylene and propylene. The thermoplastic cover films are formed by extruding onto a carrier web and laminating to a retroreflective base material. The thermoplastic cover films are sufficiently extensible to withstand substantial stretching

such as may occur during the embossing of a license plate. The materials also may serve to protect the underlying material against weathering.

FIG. 1 shows a known retroreflective sheeting 12 comprising removable protective liner 14 at the bottommost side, retroreflective element 16, pressure sensitive adhesive layer 26, polyethyleneterephtalate (PET) layer 18 with a thickness of about 25 microns and colorant/binder receptive print layer 20. Retroreflective element 16 comprises a monolayer of glass microspheres 30 embedded in a layer of polyvinyl butyral 34 with underlying reflective layer 32 and pressure sensitive adhesive layer 36. Layer 20 is directly thermally print receptive with a resin-based indicia and is formed from a composition comprising PET and a vinylidine/acrylonitrile copolymer. Sheeting material 12 (manufactured for use as an indoor product ScotchMark™ brand label stock 3929 by Minnesota Mining and Manufacturing Company, St. Paul, Minn.,) is not sufficiently frangible or durable, as defined below, for many applications.

SUMMARY OF THE INVENTION

In this invention, sheetings have been discovered which have a smooth, transparent, durable top layer, and which are directly colorant/binder receptive when a sheeting comprising a core sheet and a topmost layer of the invention is thermally printed thereon with a resin-based colorant/binder. Variable information indicia may be readily formed on sheetings comprising topmost layers of the invention, and the sheetings can be configured to have a desired combination of frangibility, retroreflectivity and enhanced durability and/or weatherability. Because topmost layers of the invention may contribute to the functional properties of polymeric sheetings, formerly provided by layers such as cover layers and/or clear coats, such topmost layers also may be referred to as multi-function layers.

In the present invention, a durable, retroreflective polymeric sheeting material is provided, which comprises: a) a multi-function layer having first and second major surfaces and a thickness of greater than about 6 microns, the multi-function layer being formed from a composition comprising a polyurethane; and b) a core sheet comprising a retroreflective layer and first and second major surfaces, the first major surface of the core sheet being attached to the first major surface of the multi-function layer; wherein the polymeric sheeting is directly thermally print receptive upon the second major surface of the multi-function layer using an indicia that contains a resin-based colorant/binder.

The present invention also provides a frangible, durable, retroreflective polymeric sheeting material, comprising: a) a multi-function layer of greater than about 6 microns in thickness formed from a composition comprising from about 70 to about 100 parts by weight aqueous dispersion of polyurethane, said multi-function layer having first and second major surfaces, the second major surface being directly thermally print receptive with an indicia that contains a resin-based colorant/binder; b) a binder layer comprising synthetic polyester resin crosslinked with a butylated melamine resin and being attached to the first major surface of the multi-function layer; c) a spacecoat layer comprising polyvinyl butyral under said binder layer; d) a monolayer of glass microspheres embedded in the spacecoat layer and in the binder layer; e) a reflective material underlying said monolayer of glass microspheres; and f) a pressure sensitive adhesive layer disposed under the reflective material.

The present invention also provides a frangible, durable, retroreflective polymeric sheeting material, comprising: a) a multi-function layer of greater than about 6 microns in thickness formed from a composition comprising from about 0 to about 60 parts by weight acrylic emulsion and about 40 to about 100 parts by weight aqueous dispersion of polyurethane, said multi-function layer having a lower surface and an exposed, upper surface; b) a binder layer comprising synthetic polyester resin crosslinked with a butylated melamine resin attached to said multi-function lower surface; c) a spacecoat layer comprising polyvinyl butyral under said binder layer; d) a monolayer of glass microspheres having bottommost and topmost surfaces, said bottommost surfaces embedded in said spacecoat layer and said topmost surfaces embedded in said binder layer; e) a reflective material underlying said monolayer of glass microspheres; and f) a pressure sensitive adhesive layer under said reflective material, said polymeric sheeting material being directly thermally print receptive upon said multi-function layer upper surface with an indicia that contains a resin-based colorant/binder. The multi-function layer may be formed from a composition comprising from about 25 to about 50 parts of weight acrylic emulsion and about 40 to about 80 parts by weight aqueous dispersion of polyurethane, which dispersion may comprise from about 45 to about 55 parts of water and from about 30 to about 40 parts of aliphatic polyurethane. The binder layer may comprise polyvinyl butyral or synthetic polyester resin crosslinked with a butylated melamine resin.

The present invention also provides a frangible, retroreflective polymeric sheeting material, comprising: a) a topmost layer having a lower surface and an exposed, upper surface, said topmost layer formed from a composition comprising polyethyleneterephtalate and vinylidine chloride/acrylonitrile copolymer; b) a cover layer attached to said lower surface; and c) a core sheet underlying said cover layer, said polymeric sheeting material being directly thermally print receptive upon said topmost layer upper surface using resin-based colorant/binder. The cover layer of the polymeric sheeting material may be less than about 10 microns in thickness and formed from a composition comprising polyethyleneterephtalate. Alternatively, the cover layer may be formed from a composition comprising an aqueous dispersion of aliphatic polyurethane and an acrylic emulsion. Such a cover layer may be formed from a composition comprising from about 40 to about 100 parts of an aqueous dispersion of polyurethane, the dispersion comprising from about 45 to about 55 parts of water and from about 30 to about 40 parts of aliphatic polyurethane, and from about 0 to about 60 parts of acrylic emulsion. Such polymeric sheeting materials may further comprise resin-based colorant/binder directly applied to the upper exposed surface of the topmost layer. The polymeric sheeting materials comprising resin-based colorant/binder may comprise a signage article. The polymeric sheeting materials less than about 125 microns in thickness may exhibit residual evidence of physical tampering when the sheeting experiences a load at break of less than about 15 pounds.

The present invention also provides a method of making a retroreflective polymeric sheeting material, comprising the steps of: a) providing a core sheet having a retroreflective layer and first and second major surfaces; b) applying a composition comprising a polyurethane onto the first major surface of the core sheet; and c) drying and curing the composition to form a multi-function layer of greater than about 6 microns in thickness having a first and second major surfaces, the first major surface being secured to the core sheet, and the major surface being directly thermally print receptive using a resin-based indicia. The polymeric sheet-

ing material of the method is directly printable using resin-based colorant/binder upon the upper exposed surface of the multi-function layer. The polyurethane composition of the method may comprise from about 70 to about 100 parts by weight aqueous dispersion of polyurethane. The composition may further comprise up to about 5 parts by weight aziridine crosslinker or about 4 parts by weight melamine crosslinker. Alternatively, the composition may comprise from about 0 to about 60 parts by weight acrylic emulsion and from about 40 to about 100 parts by weight aqueous dispersion of polyurethane. The multifunction layer of the polymeric sheeting material of the method may be from about 6 microns to about 35 microns in thickness, preferably from about 7 microns to about 25 microns in thickness, and the sheeting material may be frangible.

The present invention aim provides a method of making a polymeric sheeting material, comprising the steps of: a) providing a removable forming support; b) applying a composition comprising a polyurethane onto said removable forming support; c) drying and curing said composition to yield a multi-function layer of greater than about 6 microns in thickness having first and second major surfaces, the second major surface being disposed on said removable forming support; d) attaching a core sheet comprising a retroreflective layer to said multi-function layer first surface; e) removing said forming support and exposing the second major surface; and f) directly thermally printing an indicia upon the second major surface using resin-based colorant/binder. The composition of the method may comprise from about 70 to about 100 parts by weight aqueous dispersion of polyurethane, which dispersion comprises from about 45 to about 55 parts of water, from about 30 to about 40 parts of aliphatic polyurethane. A composition comprising an aqueous dispersion of polyurethane may further comprise up to about 5 parts by weight aziridine crosslinker or up to about 4 parts by weight melamine crosslinker. Alternatively, the composition of the method may comprise from about 40 to about 100 parts by weight aqueous dispersion of polyurethane, the dispersion comprising from about 45 to about 55 parts of water, from about 30 to about 40 parts of aliphatic polyurethane and from about 0 to about 60 parts by weight acrylic emulsion. The multi-function layer of the method may be from about 6 microns to about 35 microns in thickness, preferably from about 7 microns to about 25 microns, and the sheeting material may be frangible.

The present invention also provides a method of making a retroreflective polymeric sheeting material, comprising the steps of: a) providing a removable forming support; b) applying a composition comprising a polyurethane onto said removable forming support; c) drying and curing said composition to form a multi-function layer of greater than about 6 microns in thickness having a first and second major surfaces, the second major surface being disposed on said removable forming support; d)applying a monolayer of microspheres in a binder layer to said multi-function layer first surface, said microspheres having topmost and bottommost surfaces; e) applying a spacecoat layer comprising polyvinyl butyral to said monolayer of microspheres, wherein said microsphere topmost surfaces are embedded in said binder layer and said microsphere bottommost surfaces are embedded in said spacecoat layer; f) applying a reflective material onto said spacecoat layer; and g) removing said forming support to yield said polymeric sheeting material and expose said multi-function layer second surface; and h) thermally printing a resin-based indicia upon the second surface of the multi-function layer using a resin based colorant/binder.

Frangible, retroreflective sheeting materials often are used to make outdoor-use articles, such as vehicular validation stickers. In order to improve the durability and/or weatherability of such frangible stickers, issuing authorities generally print repeating or incrementally changing information on a core sheeting material, followed by application of a clear coat to form a finished article. Such clear coats have been desired in order to bury or embed the indicia. The invention disclosed herein allows a durable thermal printing of indicia on a frangible, retroreflective sheeting material without the need for subsequent application of a clear coat. A further advantage is that an article of the invention may have indicia embedded in the resin as well as printed on top of the article. That is, some indicia may be provided on the core sheet while other indicia are subsequently formed on the upper, exposed surface of the multi-function layer using a thermally printed resin-based colorant/binder. For example, a validation sticker may have repeating or incrementally changing indicia provided on the core sheet and variable information indicia formed on the multi-function layer.

Retroreflective polymeric sheeting materials disclosed herein are advantageous in that such sheetings allow variable information indicia to be formed without having to add a clear coat after printing to protect indicia. The production of signage articles is thereby made much more convenient, particularly the production of large numbers of variable information articles. For example, sheetings can have item-specific indicia directly printed on articles in dispersed locations without the need for such locations to have clear coating equipment and facilities.

Directly printable sheetings disclosed herein may be used to make articles upon which formed indicia are easily varied from article to article. In particular, variation in the indicia printed on an article need not be a regular incremental change in an alphanumeric sequence. Instead, indicia may be varied in an item-specific manner, for example, by selecting article-specific indicia immediately prior to printing such indicia upon an article. Article-specific indicia may be generated based upon desired input criteria, such as registration status, name of individual requesting a printed article, printing date, expiration date, product number, warehouse location and the like. Combinations of criteria may be used also, and/or separate criteria may be used to form sub-elements of the formed indicia.

Bar-coded labels or stickers often are used to identify and maintain appropriate levels of inventory, for example, in a warehouse or distribution center. In addition to the use of labels for inventory control, durable and/or weatherable articles constructed from polymeric sheetings of the invention may also be frangible, in order to inhibit theft and/or transfer of labels from one item or package to another item or package. Security also may be enhanced by forming some portions of the variable information indicia in a random or otherwise unpredictable manner. Randomized variable information indicia for labeled packages then may be maintained in a secure central information storage system to inhibit fraud or theft.

The above and other aspects of the invention are more fully shown and described in the drawings and detailed description of this invention, where like reference numerals are used to represent similar pans. It is to be understood, however, that the description and drawings are for the purposes of illustration only and should not be read in a manner that would unduly limit the scope of this invention.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 is a schematic cross-sectional view of a known retroreflective sheeting material that is thermally print receptive.

FIG. 2 is a schematic cross-sectional view of a retroreflective sheeting material in accordance with the present invention.

FIG. 3 is a cross-sectional view of a signage article in accordance with the present invention.

FIG. 4 is a top view of the signage article of FIG. 3.

FIG. 5 is a top view of a signage article in accordance with the present invention.

FIG. 6 is a cross-sectional view of an alternative embodiment of a retroreflective sheeting in accordance with the present invention.

FIG. 7 is a cross-sectional view of an alternative embodiment of a retroreflective sheeting in accordance with the present invention.

FIG. 8 is a cross-sectional view of an alternative embodiment of a retroreflective sheeting in accordance with the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF INVENTION

In describing preferred embodiments of the invention, specific terminology will be used for the sake of clarity. The invention, however, is not intended to be limited to the specific terms so selected, and it is to be understood that each term so selected includes all the technical equivalents that operate similarly.

It would be desirable to have a layer on the topmost side of a sheeting that can have the functional properties of both a cover layer (and/or other layers such as a clear coat) and a print receptive layer. Such a topmost layer, referred to below as a multi-functional layer, could contribute to the durability necessary for extended life applications, could complete optical relationships if necessary for a retroreflective sheeting, could maintain frangibility if desired, could protect the underlying components of the sheeting and/or could contribute to the stability of the overall sheeting, while also being receptive to direct printing with a resin-based ribbon. The construction of sheetings having such a layer could be simpler than many known sheetings that require multiple layers to provide the functional properties of cover layers and/or clear coats and are not directly printable using resin-based colorant/binder.

A multi-function layer should be of a thickness that is appropriate for the applications in which sheetings and articles made therefrom will be used. For example, frangible articles are desired in certain applications. As used herein, the term "frangible" means the article can be easily damaged when an attempt is made to remove, alter, or otherwise deliberately tamper with the article. Frangible articles may have low tear strength, and/or brittleness, and/or be readily stretched or deformed (i.e., strained), so that tearing, cracking, stretching or deformation (strain) provides evidence, preferably to the unaided human eye, that an attempt has been made to tamper with the article. One example of measuring frangibility is discussed below in Example 3.

Frangible polymeric sheeting materials less than about 150 microns in thickness may exhibit residual evidence of physical tampering when a portion of the sheeting experiences a load which creates 25 percent strain of that portion.

The load may be less than 7 pounds per inch of width (1.25 kilograms (kg) per centimeter (cm) of width). Frangible polymeric sheeting materials may exhibit residual evidence of physical tampering when a portion of the sheeting experiences a load at break of less than about 7 pounds per inch of width (1.25 kg per cm of width) and the sheeting is less than about 150 microns in thickness.

Durable and weatherable articles also may be formed in accordance with the present invention. As used herein, the term "durability" refers to characteristics such as solvent or chemical resistance, abrasion resistance, bond maintenance between the various layers of an article or between the indicia and the multi-function layer, and/or maintenance of retroreflective brightness under normal use conditions. As used herein, the term "weatherability" refers to characteristics such as maintenance of retroreflective brightness, resistance to dirt, resistance to yellowing and the like, all of the above under normal use conditions in the outdoors, where sunlight, temperature, and other environmental parameters may affect sheeting performance.

FIG. 2 illustrates a preferred embodiment of a retroreflective polymeric sheeting **80** of the present invention. Sheeting **80** comprises a removable protective liner **14** at the bottommost side, a core sheet that includes a representative beaded retroreflective element **62** and a multi-function layer **82**. Retroreflective element **62** comprises pressure sensitive adhesive **36**, a monolayer of microspheres **30** with underlying reflective material **32**, space coat layer **43**, and binder layer **44**.

Sheeting **80** comprising multi-function layer **82** is directly thermally print receptive using resin-based colorant/binder. Furthermore, multi-function layer **82** contributes to other functional properties of polymeric sheetings of the invention. In durable, retroreflective, sheeting material **80**, layer **82** may serve as a cover layer/clear coat. Layer **82** may complete optical relationships necessary to provide retroreflectivity. At a thickness of about 6 to about 35 microns, layer **82** may contribute to frangibility. Previously known frangible, retroreflective sheetings often used a 40 to 50 micron thick cover layer in addition to a 10 to 20 micron thick clear coat, for a total thickness of the upper layers of about 50 to about 70 microns.

The core sheet of sheeting **80** comprises retroreflective element **62** and removable protective liner **14**. However, a core sheet may comprise only element **62**, for example, when sheeting **80** is adhered to a substrate. A liner such as liner **14** may optionally be a part of a core sheet in other embodiments disclosed herein as well.

A multi-function layer should be of a thickness that is appropriate for the applications in which sheetings and articles made therefrom will be used. The multi-function layer may be from about 6 to about 35 microns in thickness, more preferably about 7 to about 25 microns in thickness. Such a thickness will contribute to durability while still retaining the frangible character of the article. A non-frangible, durable multi-function layer may be from about 20 to about 80 microns in thickness, preferably flora about 40 to about 60 microns in thickness.

A multi-function layer may be formed from a composition comprising polyurethane, for example, a water-borne dispersion of aliphatic polyurethanes, at from about 70 to about 100 parts by weight, preferably from about 80 to about 100 parts by weight. Illustrative examples of useful dispersions of polyurethane include NEOREZ™ R960 (an aqueous dispersion of aliphatic polyurethane believed to contain 53.5 parts by weight water, 33 parts aliphatic polyurethane with

a weight average molecular weight between about 100,000 and 250,000, 16.8 parts N-methylpyrrolidone, and 1.6 parts triethylamine, from Zeneca Resins, Wilmington, Mass.) and NEOREZ™ R9637 (aqueous dispersion of aliphatic polyurethane from Zeneca Resins, believed to contain 48.6 pans by weight water, 36 pans aliphatic polyurethane with a weight average molecular weight between about 100,000 and 250,000, 8.5 pans N-methylpyrrolidone, and 2.0 pans triethylamine) and NEOREZ™ R9679 (aqueous dispersion from Zeneca Resins that is believed to be somewhat similar to R9637).

Multi-function layers may be formed from compositions having one or more crosslinkers in addition to a polyurethane. Crosslinkers may increase weatherability and chemical resistance of the multi-function layer. Examples of crosslinkers are melamine and aziridine. Aziridine crosslinkers may improve the tendency of the resultant top layer to lie flat and generally do not require high temperatures to cure. Melamine crosslinkers may provide a longer pot life and shelf life and are believed to be less hazardous for shipping. Blends of crosslinkers may be used, if desired.

When melamine is used as a crosslinker, compositions used to form multi-function layers of the invention may contain up to about 4 parts melamine (typically from about 8 to 12 weight percent based on resin solids). An illustrative example of a suitable melamine crosslinker is sold under the trade name RESIMENE AQ 7550 (an aqueous solution containing 78 to 80 parts methylated melamine formaldehyde and 20 to 22 parts water) from Monsanto, St. Louis, Mo.

When aziridine is used as a crosslinker, compositions used to form multi-function layers may contain up to about 5 parts aziridine (typically from about 10 to about 17 weight percent based on resin solids), preferably 2.8 parts aziridine or less. Compositions containing aziridine crosslinkers generally exhibit shorter pot life than those containing melamine crosslinker. However, sheetings formed from such compositions can be allowed to dry and cure without special heating. An illustrative example of a suitable aziridine crosslinker is sold under the trade name CX-100, a polyfunctional aziridine, believed to be 100 percent solids, from Zeneca Corporation.

Multi-function layer compositions used herein also may contain one or more of the following added components: ultraviolet light absorber, antifoaming agent, surfactant, rheology modifier, anti-skinning, leveling agent, coloring agent, mar agent, rust inhibitor, thickener, flow agent, ultraviolet light stabilizer and biocide. Co-solvents such as N-methylpyrrolidone also may be added, for example, at up to about 4 parts by weight. Such components should be compatible with the polyurethane.

An illustrative example of a suitable UV light stabilizer is TINUVIN™ 292, a hindered amine light stabilizer containing bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate and methyl-1,2,2,6,6-pentamethyl-4-piperidinyl sebacate, from Ciba-Geigy, Ardsley, N.Y. An illustrative example of a suitable UV light absorber is TINUVIN™ 1130, containing the reaction product of beta-[3-(2H-benzotriazol-2YL-4-hydroxy-5-tert-butylphenyl)] propionic acid, methyl ester and ethylene glycol 300, from Ciba-Geigy. An illustrative example of a suitable surfactant is FLUORAD™ FC-120 fluorochemical surfactant (Minnesota Mining and Manufacturing, St. Paul, Minn.) containing 25 parts ammonium perfluoralkyl sulfonate, 37.5 parts 2-butoxyethanol, and 37.5 parts water. An illustrative example of a suitable antifoaming agent is NALCO 2343, containing 40 to 70 parts straight run middle distillates, 10 to 50 parts blend of fatty acids, polyglycols, polyglycol ester, and oxyalkylate, and 10 to 20 parts kerosene, from Nalco Company, Chicago, Ill.

An embodiment of a composition that comprises an aqueous dispersion of a polyurethane, an aziridine crosslinker, a UV light stabilizer, a UV light absorber, surfactant, and antifoaming agent may comprise, for example, about 94.83 parts NEOREZ™ R960, 2.84 parts CX-100 aziridine crosslinker, about 0.63 parts TINUVIN™ 292 UV stabilizer, about 0.95 parts TINUVIN™ 1130 UV absorber, about 0.63 parts N-methyl pyrrolidone, about 0.03 parts Fluorad™ fluorochemical surfactant FC-120, and about 0.09 parts Nalco 2343 anti-foaming agent.

An alternative composition forming a multi-function layer of the invention may comprise an aliphatic polyurethane dispersion and an acrylic emulsion, for example, of polymethyl methacrylate. Multi-function layers formed from compositions comprising an aliphatic polyurethane and an acrylic emulsion generally cost less than compositions without acrylic emulsions. An illustrative example of an acrylic emulsion is NEOCRYL™ A-612 (an acrylic emulsion from Zeneca containing about 32 weight percent solids, 28.9 volume percent solids, about 54 weight percent water, and about 13.8 weight percent volatile organic compounds). Other illustrative emulsions include NEOCRYL™ A-601 and A-614. The emulsion preferably does not contain polystyrene. Multi-function layers made from compositions containing styrenated emulsions generally are not as weatherable as well as those containing emulsions that are not styrenated. The proportions of polyurethane and acrylic emulsion may be varied to suit the particular application in which the polymeric sheeting material is used. For example, the proportion of acrylic emulsion may be adjusted to achieve the desired brittleness of a multi-function layer (which enhances the frangibility of sheeting materials), to confer the desired level of adhesion to a particular core sheet, or to achieve the desired durability of the polymeric sheeting material. Suitable proportions can be determined by those skilled in the art and may be, for example, from greater than about 0 to about 60 parts acrylic emulsion and from about 40 to about 100 parts polyurethane, preferably from about 20 to about 50 parts acrylic emulsion and from 40 to about 80 parts polyurethane. Multi-function layers formed from compositions comprising a polyurethane dispersion and an acrylic emulsion preferably do not contain a crosslinker, because urethane/acrylic/crosslinker compositions generally do not form multi-function layers that are directly thermally printable with resin-based colorant/binder.

An embodiment of a polymeric sheeting material having a multi-function layer formed from a composition comprising an aqueous polyurethane dispersion and an acrylic emulsion is a composition comprising about 48.9 parts NEOREZ™ R9637 aliphatic polyurethane dispersion, about 48.9 parts NEOCRYL™ A-612 acrylic emulsion, about 0.6 parts TINUVIN™ 292 UV stabilizer, about 1.0 parts TINUVIN™ 1130 UV absorber, and about 1.0 parts N-methyl pyrrolidone.

Retroreflective polymeric sheeting in the core sheet may be, for example, "beaded sheeting" in the form of an encapsulated-lens sheeting (see, for example, U.S. Pat. Nos. 3,190,178; 4,025,159; 4,896,943; 5,064,272; and 5,066,098, the disclosures of which are incorporated here by reference), enclosed-lens sheeting (see, for example, U.S. Pat. No. 2,407,680, the disclosure of which is incorporated here by reference), or may comprise a cube corner retroreflective sheeting (see, for example, U.S. Pat. Nos. 3,684,348; 4,801,

193; 4,895,428; and 4,938,563, the disclosures of which are incorporated here by reference).

For example, in one embodiment of the invention the core sheet may comprise a binder layer at the topmost side, a spacecoat layer comprising polyvinyl butyral under the binder layer, a monolayer of microspheres having bottommost and topmost surfaces, the bottommost surfaces embedded in the spacecoat layer and the topmost surfaces embedded in the binder layer, a reflective material underlying the monolayer of microspheres and a pressure sensitive adhesive layer at the bottommost side. The binder layer may comprise, for example, a polyvinyl butyral or a synthetic polyester resin crosslinked with a butylated melamine resin. The thickness of the binder layer typically is about 20 to 120 microns thick. The microspheres typically are made of glass, have refractive indices of about 2.1 to 2.3, and have diameters ranging from about 30 to 200 microns, preferably averaging about 60 microns in diameter. The microspheres generally are embedded about 50 percent in the binder layer. The spacecoat layer typically has a thickness extending from the surface of the microsphere of approximately one fourth the average diameter of the microspheres. The reflective material may be a layer of metal flakes or vapor or chemically deposited metal layer such as aluminum or silver.

One method of forming a multi-function layer as part of a retroreflective polymeric sheeting material comprises:

a) providing a core sheet comprising retroreflective elements;

b) applying an aqueous composition comprising a polyurethane onto the core sheet; and

c) drying and curing the composition to yield a polymeric sheeting material having a multi-function layer.

The method may be used to form a multi-function layer on any of a variety of core sheets, some of which may be retroreflective, such as encapsulated-lens, enclosed-lens, cube corner elements, and the like. A core sheet initially may be retroreflective, or it may provide retroreflection only after formation of the multi-function layer. The core sheet of a retroreflective sheeting material generally comprises a number of retroreflecting elements such as microspheres with associated specularly reflective layers or cube corner elements (such as microcube corner arrangements), typically arranged in a monolayer. In some instances, a core sheet may comprise indicia formed on the top side of the sheet. Such indicia are embedded underneath the multi-function layer in the polymeric sheeting material.

An advantage of the invention is that the multi-function layer compositions can be applied to a core sheet using many convenient techniques, including for example, dipping, spraying, flood coating, curtain coating, roll coating, bar coating, knife coating, wire-wound coating, gravure coating, or laminating to deposit a preferably continuous layer of coating composition on the surface of the core sheet. Persons skilled in the art can readily select one of these or other suitable application methods for specific uses. Polyurethane compositions useful in the invention do not have to be extruded to form multi-function layers. An advantage of the invention is that the relatively long pot life of multi-function layer compositions of the invention enables use of a variety of convenient application techniques without restrictions encountered with previously used coating compositions.

After application to the core sheet, the composition is dried and cured to make a polymeric sheeting material having an upper, exposed surface formed by the multi-function layer. Depending upon the nature of the composition, drying and curing may be performed at room temperature or at slightly elevated temperature without the use of special ovens or hoods. A multi-function layer may be formed in separate operations, if desired, by, for example, forming a first portion of the multi-function layer, allowing the first portion to dry and cure, and then repeating the process to form second and subsequent portions, all portions being considered part of the multi-function layer.

Multi-function layer compositions are advantageous in that polymeric sheeting materials may now be constructed with a single layer that not only contributes to functional properties formerly requiring multiple layers such as cover layers, clear coats and the like, but furthermore is directly printable using resin-based colorant/binder. The construction of sheetings by the methods of the invention may be greatly simplified. Preferred multi-function layer compositions described herein also offer other processing advantages, including being less flammable, being considered environmentally safer, and presenting less objectionable odor because they tend to have a lower volatile organic solvent content.

Alternatively, a polymeric sheeting material comprising a multi-function layer of the invention can be made by the steps of:

a) providing a removable forming support;

b) applying a composition comprising a polyurethane onto the removable forming support; and

c) drying and curing the composition as described above to yield a multi-function layer.

The multi-function layer has a second surface disposed on the forming support and a first, exposed surface that is directly thermally printable with resin-based colorant/binder. The forming support has release properties that allow it to be removed and to expose the upper surface of the multi-function layer.

The method further comprises attaching a core sheet to the first surface of the multi-function layer and removing the forming surface support to make a retroreflective polymeric sheeting material. Such a sheeting material has the second surface of the multi-function layer exposed, and is directly thermally printable on the second surface. If desired, the attaching step may be carried out by providing an intermediate adherence layer between the core sheet and the multi-function layer. As indicated above, the core sheet may comprise encapsulated-lens, enclosed-lens, or cube corner retroreflective elements. For example, a core sheet may be comprised of encapsulated-lens retroreflective elements such as those described in U.S. Pat. No. 5,066,098, with a multi-function layer of the invention being the upper surface of the polymeric sheeting material. If desired, a retroreflective sheeting may be formed on the preformed multi-function layer, for example, by arranging a monolayer of microspheres in polymeric binder material, forming a space coat, and applying a reflector layer thereon. The indicia formed from resin-based colorant/binder may be thermally printed on the multi-function layer upper surface before or after attachment to the core sheet.

It may be desired to further increase the frangibility of sheeting materials disclosed herein, as generally described above and as particularly illustrated in Example 3. This may be done by an additional step modifying the retroreflective sheeting by, for example, exposing the sheeting to ultraviolet light or heat to increase sheeting brittleness.

The polyurethane dispersions discussed herein may contain some organic solvents, typically about 8 to 10 weight percent or less as co-solvents to facilitate mixing, handling and film formation. This limited quantity of solvent is much less than the amount of solvent used in many compositions

heretofore. Previously used compositions sometimes contained approximately 60 to 70 weight percent or more of organic solvent.

Resin-based colorant/binder can be thermally applied directly to the exposed surface of the multi-function layer of sheetings disclosed herein. The result is indicia, generally informational, adhering to an upper portion of the sheeting, which in combination produces an article. Such articles may or may not be combined with additional components to create signage articles such as traffic control materials, retroreflective vehicle markings, retroreflective garments, indoor/outdoor labeling products, frangible security stickers, product authentication products, inventory labeling and control products, identification systems, or license plates.

Suitable means for transferring colorant/binder to a polymeric sheeting of this invention may include inkjet printing systems (including solid inkjet systems) and thermal transfer printing systems or a combination of such systems as in the thermally activated valves of an inkjet system. In the context of this invention, "thermal printing" means those processes which transfer resin-based colorant/binder to a polymeric sheeting by localized heat such as in the above-described systems. "Thermally print receptive" means the substrate (viz., multi function layer) is capable of being thermally printed thereon such that the resulting indicia is durable and has a quality that displays the intended image. Colorant/binder may be transferred by means of resistive elements, ribbon-contacting elements in a laser system, electronic elements, thermally activated valve elements, inductive elements, thermopile elements, and the like. Inkjet and thermal printing apparatuses suitable for use in this invention are referred to in copending U.S. application Serial No. 08/186,752, filed Feb. 2, 1994, entitled "System And Method For Manufacturing Improved Data Display Retroreflective Sheeting, and incorporated here by reference.

A preferred means of transferring colorant/binder comprises heatable resistive elements in a thermal mass transfer printing system. Colorant/binder for use with thermal mass transfer printers generally is provided on a carrier or support, such as a ribbon. Carriers may have additives such as wetting or dispersing aids, defoamers, viscosity modifiers, leveling agents and coalescing agents. Binders carry colorant and hold colorant to the substrate sheeting after colorant is transferred. The type of binder determines whether or not the carrier will be termed wax-based, resin-based, or combination thereof.

Binders may comprise waxes such as paraffin, microcrystalline wax, beeswax, candelilla, ozocerite, or carbowax and the like. Waxes are low-melting organic mixtures or compounds of high molecular weight, solid at room temperature, and generally similar in composition to fats and oils, except that they contain no glycerides. Waxes are thermoplastic, but since they are not high polymers, they are not considered to be in the family of plastics. The thermoplastic properties of waxes make them excellent candidates for binders, since they tend to have sharp melting points, and are low in viscosity in the molten state. This allows colorant/binder to flow readily into paper fibers or onto films. Waxes are useful for printing, except that transferred wax-based colorant/binder may smear and scratch off of printed articles.

Other polymers may be substituted for waxes. Such binders generally are called resin-based binders. Resin binders in general do not have sharp melting points as waxes do, but they are tougher and do not smear or scratch like waxes. Resin-based colorant/binders may have some proportion of wax binders, for example, 5 weight percent or less, in order to adjust certain properties such as flow characteristics.

Sheetings comprising multi-function layers made from compositions disclosed herein are receptive to resin-based colorant/binder. The adhesion of colorant/binder to a particular sheeting and the quality of resulting indicia will vary somewhat among various resin-based colorant/binders.

The upper surface of retroreflective sheetings comprising multi-function layers preferably is sufficiently smooth to allow transfer of resin-based colorant/binder to the upper surface. The colorant/binder receptivity provided by multi-function layers greater than about 6 microns was surprising, because known cover layers generally are not receptive to a thermally printed resin-based colorant/binder or have unacceptable print quality. Further, polyurethane-containing prime layers about 2 microns thick generally are not thermally printable with resin-based colorant/binder. It was not expected that a polyurethane-containing layer greater than about 6 microns would behave significantly different from a 2 micron thick prime layer.

When using a thermal mass transfer printing system to apply indicia to the multi-function layer, the means for transferring colorant/binder preferably comprises a resin-based ribbon. When a wax-based ribbon is used to form indicia on the surface of a polymeric sheeting material, it is well-known in the art that a layer such as a clear coat generally must be applied to protect the indicia, as wax-based indicia are very susceptible to normal wear and tear or to damage when scratched. It has been difficult to achieve adherence of colorant/binder from resin-based ribbons to many retroreflective polymeric sheeting materials, a difficulty that has been overcome by the present invention.

An embodiment of a signage article is shown schematically in cross-section in FIG. **3**, and in a top view in FIG. **4**. Signage article **120** comprises indicia **122** and a core sheet that includes a retroreflective polymeric sheeting material **62** as described above. Indicia **122** may be formed from a resin-based colorant/binder, and multi-function layer **82** may be formed from, for example, a composition comprising an aqueous polyurethane dispersion. FIGS. **3** and **4** illustrate indicia **122** disposed above the topmost surface; however, a retroreflective article of the invention also may have the indicia located underneath the multi-function layer— although this is not necessary in some embodiments because in accordance with the invention an exposed resin-based indicia can be provided which is sufficiently durable by itself and therefore need not be buried in the signage article. As indicated above, variable thermally-printed indicia now may be durably printed on a polyurethane top surface of a retroreflective sheeting.

Another embodiment of a signage article is shown in top view in FIG. **5**. Article **130** comprises indicia **132** and a polymeric retroreflective sheeting material similar to sheeting **80** shown in FIG. **2**. A resin-based colorant/binder can form indicia **132**, and the multi-function layer may be comprised of an aqueous polyurethane dispersion and an acrylic emulsion.

FIG. **6** schematically illustrates another embodiment of a frangible, retroreflective polymeric sheeting material. Sheeting material **22** comprises removable protective liner **14**, retroreflective element **16**, pressure sensitive adhesive layer **26**, thin layer **38**, and colorant/binder-receptive print layer **39**. Thin layer **38** generally is less than 10 microns in thickness and preferably about 6 microns in thickness. Thin layer **38** may be comprised of PET. Topmost layer **39** and thin PET layer **38** may be readily obtained as preformed product AZ SLP 31393, from Process Label Corporation, Minneapolis, Minn., and may be subsequently attached to adhesive layer **26**. The underlying liner then is stripped off,

and the conjoined layers **39**, **38** and **26** are attached to the remainder of the sheeting material layers, for example, by laminating them.

The ability to form and adhere layers **39**, **38** and **26** to the remainder of the sheeting material layers to form sheeting **22** was unexpected, due to the thinness of conjoined layers **39**, **38** and **26**. The fact that sheeting material **22** can be constructed at all allows articles to be made for applications in which enhanced frangibility and direct printability are desired.

A topmost layer **39** in accordance with the invention may comprise PET and a vinylidine chloride/acrylonitrile copolymer, for example, Goodyear "Vitel™ PE222 PET and Dow Saran™ 310F vinylidine chloride/acrylonitrile copolymer. Compositions used to form such print layers may range from 0 to 100 percent PET and from 100 to 0 percent vinylidine chloride/acrylonitrile copolymer.

The frangibility of sheeting **22** is at least partially due to the thinness of layer **38**. Although layer **38** is made of relatively low cost materials such as PET, it would be desirable to simplify the construction of frangible sheeting materials and further, to construct frangible sheeting materials having enhanced durability and/or weatherability.

Frangible sheetings having receptivity to direct thermal printing of resin-based colorant/binder are shown in FIGS. **7** and **8**.

In reference to FIG. **7**, polymeric sheeting material **60** comprises removable protective liner **14**, retroreflective element **62**, and a topmost layer **54** which is directly thermally print receptive to a resin-based colorant/binder. Retroreflective element **62** comprises pressure sensitive adhesive **36**, a monolayer of glass microspheres **30** with underlying reflective layer **32**, space coat layer **43** and synthetic polyester/butylated melamine resin binder layer **44**. Topmost layer **54** can be formed from a composition comprising about 7.5 percent Goodyear "Vitel™ PE222 polyethyleneterephtalate and about 1.9 percent Dow Saran™ 310F vinylidine chloride/acrylonitrile copolymer. Sheeting **60** is simpler to manufacture while still providing retroreflectivity, frangibility, and direct thermal printing using resin-based colorant/binder.

FIG. **8** illustrates a frangible, retroreflective polymeric sheeting material that has good durability. Sheeting **70** comprises a removable protective liner **14**, retroreflective element **62**, cover layer **72**, and colorant/binder-receptive topmost layer **54**. Cover layer **72** may be formed from a composition comprising an aqueous dispersion of an aliphatic polyurethane and an acrylic emulsion. An illustrative example is a composition comprising about 47.4 percent Neorez™ R-9637 water-borne aliphatic urethane dispersion, about 47.4 percent Neocryl™ A-612 water-borne acrylic emulsion, about 3.6 percent N-methylpyrrolidone, about 0.6% TINUVIN™ 292, and about 1.0 percent TINUVIN™ 1130. Surprisingly, cover layer **72** adheres to binder layer **44** and topmost layer **54** adheres to cover layer **72**. Cover layer **72** enhances durability and also may complete optical relationships needed for retroreflective sheeting material **70**. Directly thermally print receptive sheetings as disclosed in FIG. **8** are useful, and may be configured to provide the desired combination of frangibility and retroreflectivity. Such sheetings may have enhanced durability and/or weatherability.

The above described embodiments of frangible retroreflective sheetings preferably employ an adhesive that provides a peel strength to a substrate which exceeds the bond strength between the various layers of the articles. In this way, the article can be rendered frangible (for example, becomes fractured or distorted) when an attempt is made to remove the article from the substrate. Typically, the adhesive is a pressure sensitive adhesive (PSA) such as a conventional PSA that comprises isooctylacrylate and acrylic acid.

Features and advantages of this invention are shown in the following illustrative Examples, selected for showing various embodiments of the invention in detail. It should be understood, however, that while the Examples serve this purpose, the particular amounts and ingredients recited therein, as well as other conditions and details, should not be construed to unduly limit the scope of this invention. Unless otherwise indicated, all amounts are expressed in the Examples are in weight percent.

EXAMPLE 1

This Example discloses polymeric sheeting materials that have a multi-function layer formed from a composition comprising polyurethane with or without crosslinker, and that are directly thermally print receptive using resin-based colorant/binder. The compositions from which the various multi-function layers (MFL) were formed are shown in Table 1.

TABLE 1

	Composition Of Urethane Multi-Function Layers (MFL) With And Without Crosslinker									
MFL	R960[a]	R9637[b]	Azir[c]	Melam[d]	UV Stab[e]	UV Abs.[f]	NMP[g] Coslv	Surf[h]	AntiFoam[i]	Water
U1	100.0									
U2	97.9				0.59	0.88	0.59			
U3		100.0								
U4		98.7			0.60	1.00	1.00			
UX1		95.79	1.85		0.67	1.02	0.67			
UX2	96.06		1.70		0.64	0.96	0.64			
UX3	91.43			3.41	0.61	0.91	0.61	0.02	0.05	2.96
UX4	94.17			3.51	0.63	0.94	0.63	0.03	0.09	
UX5	91.70		0.92	0.50	0.61	0.92	0.61	0.03	0.15	4.56
UX6	94.83		2.84		0.63	0.95	0.63	0.03	0.09	
UX7		94.62	2.84		0.69	1.04	0.69	0.03	0.09	
UX8	93.11		4.93		0.56	0.84	0.56			
UX9	96.25		1.73		0.58	0.87	0.58			
UX10	97.37		0.58		0.58	0.88	0.58			

[a]NEOREZ R960, water-borne aliphatic urethane dispersion, Zeneca Resins
[b]NEOREZ R937, water-borne aliphatic urethane dispersion, Zeneca Resins
[c]CX-100 Aziridine crosslinker, Zeneca Resins

TABLE 1-continued

Composition Of Urethane Multi-Function Layers (MFL) With And Without Crosslinker										
MFL	R960[a]	R9637[b]	Azir[c]	Melam[d]	UV Stab[e]	UV Abs.[f]	NMP[g] Coslv	Surf[h]	AntiFoam[i]	Water

[d]Resimene ™ AQ7550 melamine crosslinker, Monsanto
[e]Tinuvin ™ 292, hindered amine, UV stabilizer, Ciba Geigy
[f]Tinuvin ™ 1130 UV light absorber, Ciba Geigy
[g]N-methylpyrrolidone coalescing solvent
[h]Fluorad ™ FC-120 fluorochemical surfactant, 3M Company
[i]Nalco 2343 ™ antifoaming agent, Nalco Chemical

Test articles having multi-function layers formed from the compositions shown in Table 1 were prepared by notched bar or roll coating onto a core sheet and were allowed to dry and cure for about 5 minutes or less at room temperature, followed by heating for about 5 minutes at about 200° F. Compositions having melamine crosslinker received an additional 2 to 4 minutes at 300° F.

Some of the test articles (indicated as "A" in Table 2) in this Example had core sheet A on the bottommost side of the multi-function layer. Core sheet A comprised substantially a monolayer of glass microspheres having an average diameter of about 60 microns embedded in a layer of polyvinyl butyral that comprised polyvinyl butyral resin crosslinked through its hydroxyl groups to a substantially thermoset state and also contained a plasticizer. Underlying and spaced from the microspheres in the polyvinyl butyral was a specularly reflective layer. Underlying the reflective layer was a pressure sensitive adhesive layer, and a removable protective liner at the bottom.

Test articles (indicated as "B" in Table 2) had core sheet B, which comprised a binder layer of synthetic polyester resin crosslinked with a butylated melamine resin, a monolayer of glass microspheres whose topmost surfaces were embedded in the binder layer and bottommost surfaces were embedded in the spacecoat layer, a spacecoat layer of polyvinyl butyral, a reflector layer underlying and spaced from the microspheres by the spacecoat layer, a pressure sensitive adhesive layer, and a removable protective liner at the bottom.

Direct printability of the polymeric sheeting materials was evaluated by passing test articles through a TEK Bar Code Printer B-400™ or a Zebra 140™ thermal mass transfer printer in such a way as to test for printability of the upper surface of the multi-function layer. Printability was tested with a resin-based ribbon (R-1, from Japan Pulp and Paper Company (JPP-R1)) at a temperature setting of 18 and with moderate print head pressure. Printability was also tested with the same R-1 ribbon at a temperature setting of 22 and with high print head pressure. A Zebra 5099 resin-based ribbon (Zebra Company) was tested at a temperature setting of 18 and with moderate print head pressure. The test pattern was vertical and horizontal bar codes, and/or a block printing area of alphanumeric characters. Test articles were about 5 centimeters by 40 centimeters or larger.

Print quality was assessed visually for edge resolution, continuous coverage of colorant/binder, and density of the printed indicia by at least 2 people. Print quality was scored on a scale of 1 to 10, with 10 representing the best overall quality. If no colorant/binder or very little colorant/binder adhered to the article, the article was considered not printable, and print quality was scored as zero. A rating of 1 to 3 represented an unsatisfactory overall appearance of the printed indicia. A rating of 4 indicated minimally acceptable print quality. A rating of 5 or greater was considered preferable, with a rating of 6 or greater more preferable. Colorant/binder adhesion was evaluated by robbing a Faber-Castell "Magic-Rub™ 1054 or equivalent eraser over the surface of the article, and the number of eraser strokes required for visually discernible removal of the colorant from the top side of the article was noted. The results of the printing tests are shown in Table 2.

TABLE 2

			JPP R-1-Ribbon High Pressure		JPP R-1-Ribbon Moderate Pressure		Zebra 5099-Ribbon Moderate Pressure	
Core Sheet	MFL	Thickness (Microns)	Print Quality	Eraser Strokes	Print Quality	Eraser Strokes	Print Quality	Eraser Strokes
A	U1	55	9	11	9	14	4	9
A	U2	55	8	11	N.D.	N.D.	5	7
B	U3	50	7	10	7	10	5	8
B	U3	40	8	9	7	9	5	7
B	U3	20	7	10	6	12	5	7
B	U4	50	8	8	8	12	6	7
A	UX1	62	6	N.D.	N.D.	N.D.	N.D.	N.D.
A	UX2	62	9	N.D.	N.D.	N.D.	N.D.	N.D.
A	UX3	37	4	N.D.	N.D.	N.D.	N.D.	N.D.
A	UX4	25	5	12	4	9	3	6
A	UX5	25	6	10	5	10	3	6
A	UX6	35	7	10	6	12	3	8
B	UX6	25	8	12	7	13	5	10
A	UX6	35	7	7	6	9	3	5
A	UX7	35	6	10	5	12	3	8
A	UX8	75	6	11	5	15	0	N.D.
A	UX9	70	8	11	8	13	1	7

TABLE 2-continued

			JPP R-1-Ribbon High Pressure		JPP R-1-Ribbon Moderate Pressure		Zebra 5099-Ribbon Moderate Pressure	
Core Sheet	MFL	Thickness (Microns)	Print Quality	Eraser Strokes	Print Quality	Eraser Strokes	Print Quality	Eraser Strokes
A	UX10	75	9	10	8	12	3	8

N.D. = Not Done

The data set forth in Table 2 demonstrate that retroreflective sheetings of the invention are directly thermally print receptive to resin-based binders and are capable of forming durable resin-based indicia.

EXAMPLE 2

This example discloses polymeric sheeting materials that have a multi-function layer formed from compositions comprising a polyurethane dispersion and an acrylic emulsion that is directly printable. The compositions used to form the various multi-function layers are shown in Table 3.

TABLE 3

Composition of Urethane/Acrylic Multi-Function Layers With And Without UV Stabilizer Or UV Absorber

MFL	R9637[a]	A612[b]	UV Stab[c]	UV Abs.[d]	NMP Cosolv[e]
B2	50	50			
B3	48.9	48.9	0.6	1	1

[a]NEOREZ R937, water-borne aliphatic urethane dispersion, Zeneca Resins
[b]Zeneca Neocryl A612, a water-borne acrylic emulsion, Zeneca Resins
[c]Tinuvin ™ 292, hindered amine, UV stabilizer, Ciba Geigy
[d]Tinuvin ™ 1130 UV light absorber, Ciba Geigy
[e]N-methylpyrrolidone coalescing solvent

Test articles having multi-function layers MFL formed from compositions B2 and B3 were prepared as described in Example 1. Test articles were evaluated for direct printability with resin-based ribbons as described in Example 1. The results are shown in Table 4.

EXAMPLE 3

A test article was evaluated on a Sintech tensile tester for break load, percent strain at break, and load at 25 percent strain. One article comprised a core sheet B without the liner and a multi-function layer formed from a composition like B3 of Table 1, except that N-methylpyrrolidone was added at 3.6 parts by weight. Another test article comprised core sheet A without a liner and a multi-function layer formed from composition U1 shown in Table 1. Triplicate samples of each test article were evaluated. Samples had a width of 2.54 cm. The results are set forth in Table 5.

TABLE 4

			JPP R-1 High Pressure		JPP R-1 Moderate Pressure		Zebra 5099 Moderate Pressure	
Core Sheet	MFL	Thickness (Microns)	Print Quality	Eraser Strokes	Print Quality	Eraser Strokes	Print Quality	Eraser Strokes
B	B2	37	6	10	5	12	4	7
B	B3	40	7	12	6	10	5	10
B	B3	12	6	11	N.D.	N.D.	N.D.	N.D.
B	B3	12	7	10	5	7	4	7
A	B3	7	6	9	5	9	4	7

N.D. = Not Done

The data in Table 4 demonstrate that retroreflective sheetings of the invention are directly thermally print receptive to resin-based binders and are capable of forming durable resin-based indicia.

TABLE 5

Measures Of Test Article Frangibility							
Core Sheet	MFL	Resin Printable	Frangible	Thickness[d]	Break Load[a]	Strain at Break (%)[b]	Load at 25% Strain[a]
B	B3'	Yes	Yes	125	4.7	13.2	—[c]
B	B3'	Yes	Yes	125	2.8	15.3	—[c]
B	B3'	Yes	Yes	125	5.1	25.2	5.2
A	U1	Yes	Yes	104	3.6	75	4.1
A	U1	Yes	Yes	99	3.5	125	3.4
A	U1	Yes	Yes	101	4.0	143	3.2

[a]Force in lbs.
[b]Length at break/length at start, in percent
[c]Test article broke before reaching 25 percent strain
[d]Approximate thickness of entire test article in microns

The data set forth in Table 5 demonstrate that the retroreflective sheetings of the invention are frangible.

EXAMPLE 4

Polymeric sheeting materials were tested for durability and/or weatherability. Compositions used to form multi-function layers are shown in Table 6.

Test articles were evaluated by exposing them on an outdoor deck in Florida for approximately 12 months. The brightness of the articles was measured at the start and at the end of the exposure period with a retroluminometer as described in U.S. Defensive Publication T987,003 at an observation angle of 0.2° and an entrance angle of −4.0°. Sixty degree gloss was measured with a 60° glossmeter in a manner similar to ASTM D523-85. Articles were tested in duplicate. Percent of initial brightness and gloss were determined for each sample by dividing the end values by the start values (× 100). The results are shown in Table 7.

TABLE 6

Composition of Multi-Function Layers Tested for Durability/Weatherability									
MFL	R960[a]	R9637[b]	Acryl A612	UV Stab[c]	UV Abs.[d]	NMP Coslv[e]	Surf.[f]	Water	Ethanol
U10	89.1						0.1	8.1	2.7
B4		47.4	47.4	0.6	1.0	3.6			
B5		48.2	48.2			3.6			

[a]NEOREZ R960, water-borne aliphatic urethane dispersion, Zeneca Resins
[b]NEOREZ R937, water-borne aliphatic urethane dispersion, Zeneca Resins
[c]Tinuvin ™ 292, hindered amine, UV stabilizer, Ciba Geigy
[d]Tinuvin ™ 1130 UV light absorber, Ciba Geigy
[e]N-methylpyrrolidone coalescing solvent
[f]Fluorad ™ FC-120 (leveling/wetting agent), 3M [0.03]; Nalco 2343, antifoaming agent, Nalco Chemical [0.07] (these are both generically called "surfactants")

The polymeric sheeting materials were configured as shown in Table 7. The core sheet for one test article comprised core sheet A described in Example 1, a cover layer of ethylene/acrylic acid and a prime layer. This test article had a multi-function layer formed from composition U10. The core sheet for two other of test articles comprised core sheet B; one had a multi-function layer formed from composition B4, and the other of the two had a multi-function layer formed from composition B 5.

TABLE 7

Measurement Of Durability/Weatherability										
					Brightness[a]			60° Gloss		
Core Sheet	Cover Layer	Prime Layer	MFL	Thickness[b]	Start	End	%	Start	End	%
A	EAA	UX13	U10	20	85	66	78	93	83	89
A	EAA	UX13	U10	20	84	68	81	94	87	93
B	—	—	B4	18	95	68	72	80	59	74
B	—	—	B4	18	95	68	72	80	60	75
B	—	—	B5	20	95	27	29	84	59	70
B	—	—	B5	20	98	29	29	84	57	68

[a]Candela/lux/meter^2
[b]Approximate thickness of the topmost layer in microns

The data in Table 7 demonstrate that the multi-function layers of the invention are durable and weatherable.

Various modifications and alterations of this invention will become apparent to those skilled in the an without departing from the scope and spirit thereof. It should be understood, therefore, that the scope of this invention is not to be limited to the illustrative embodiments set forth herein, but is to be determined by the limitations set forth in the claims and equivalents thereof.

What is claimed is:

1. A durable, retroreflective polymeric sheeting comprising:

(a) a frangible multi-functional layer having first and second major surfaces and a thickness of greater than about 6 microns, the multi-functional layer being formed from a composition comprising a polyurethane; and

(b) a core sheet having first and second major surfaces, the first major surface of the core sheet being attached to the first major surface of the multi-functional layer, said core sheet comprising in order:

1) a binder layer at said first major surface of said core sheet;

2) a spacecoat layer comprising polyvinyl butyral under said binder layer;

3) a monolayer of microspheres having bottommost and topmost surfaces, said bottommost surfaces embedded in said spacecoat layer and said topmost surfaces embedded in said binder layer;

4) a reflective material underlying said monolayer of microspheres; and

5) a pressure sensitive adhesive layer at said bottommost surface underlying said reflective material; wherein

the polymeric sheeting is directly thermally print receptive upon the second major surface of the multi-functional layer using an indicia that contains a resin-based colorant/binder.

2. The polymeric sheeting material of claim 1, further comprising a thermally printed indicia disposed on the second major surface of the multi-function layer, the thermally printed indicia comprising a resin-based colorant binder.

3. The polymeric sheeting material of claim 1, wherein said binder layer is formed from a composition comprising synthetic polyester resin crosslinked with a butylated melamine resin.

4. The polymeric sheeting material of claim 1, wherein said multi-function layer is less than 35 microns in thickness and said sheeting material is frangible.

5. The polymeric sheeting material of claim 1, wherein said multi-function layer is formed from a composition comprising an aqueous aliphatic polyurethane dispersion.

6. The polymeric sheeting material of claim 6, wherein said multi-function layer is formed from a composition comprising from about 70 to about 100 parts by weight aqueous dispersion of polyurethane, said dispersion comprising from about 40 to about 60 parts of water and from about 20 to about 60 parts of aliphatic polyurethane.

7. The polymeric sheeting material of claim 6, wherein said multi-function layer is formed from a composition comprising from about 70 to about 100 parts by weight aqueous dispersion of polyurethane, said dispersion comprising from about 45 to about 55 parts of water and from about 30 to about 40 parts of aliphatic polyurethane.

8. The polymeric sheeting material of claim 5, wherein said multi-function layer composition further comprises up to about 5 parts by weight aziridine crosslinker.

9. The polymeric sheeting material of claim 5, wherein said multi-function layer composition further comprises up to about 4 parts by weight melamine crosslinker.

10. The polymeric sheeting material of claim 5, wherein said multi-function layer is formed from a composition comprising:

a) from about 40 to about 100 parts by weight aqueous dispersion of polyurethane, said dispersion comprising from about 40 to about 60 parts of water and from about 20 to about 60 parts of aliphatic polyurethane; and

b) from about 0 to about 60 parts by weight acrylic emulsion.

11. The polymeric sheeting material of claim 10, wherein said multi-function layer is formed from a composition comprising;

a) from about 40 to about 100 parts by weight aqueous dispersion of polyurethane, said dispersion comprising from about 45 to about 55 parts of water and from about 30 to about 40 parts of aliphatic polyurethane; and

b) about 0 to about 60 parts by weight acrylic emulsion.

12. The polymeric sheeting material of claim 1, further comprising resin-based colorant/binder directly applied to said multi-function layer upper surface.

13. The polymeric sheeting material of claim 12, wherein said sheeting material comprises a signage article that has a thermally printed indicia disposed on the second major surface of the multi-function layer, the thermally printed indicia comprising a resin-based binder system.

14. A signage article according to claim 13, wherein said multi-function layer is from about 6 microns to about 35 microns in thickness and said article is frangible.

15. A frangible, durable, retroreflective polymeric sheeting material, comprising:

a) a frangible multi-function layer of greater than about 6 microns in thickness formed from a composition comprising from about 70 to about 100 parts by weight aqueous dispersion of polyurethane, said multi-function layer having first and second major surfaces, the second major surface being directly thermally print receptive with an indicia that contains a resin-based colorant/binder;

b) a binder layer comprising synthetic polyester resin crosslinked with a butylated melamine resin and being attached to the first major surface of the multi-function layer;

c) a spacecoat layer comprising polyvinyl butyral under said binder layer;

d) a monolayer of glass microspheres embedded in the spacecoat layer and in the binder layer;

e) a reflective material underlying said monolayer of glass microspheres; and

f) a pressure sensitive adhesive layer disposed under the reflective material.

16. The polymeric sheeting material of claim 15, wherein said multi-function layer is formed from a composition comprising from about 90 to about 100 parts of weight aqueous dispersion of polyurethane, said dispersion comprising about 45 to about 55 parts of water and from about 30 to about 40 parts of aliphatic polyurethane.

17. A frangible, durable, retroreflective polymeric sheeting material, comprising:

a) a frangible multi-function layer of greater than about 6 microns in thickness formed from a composition comprising from about 70 to about 100 parts by weight aqueous dispersion of polyurethane, said multi-function layer having a lower surface and an exposed, upper surface;

b) a layer comprising polyvinyl butyral attached to said multi-function layer lower surface;

c) a monolayer of glass microspheres embedded in said polyvinyl butyral layer;

d) a reflective material underlying said monolayer of glass microspheres; and

e) a pressure sensitive adhesive layer under said reflective material, said polymeric sheeting material being directly thermally print receptive upon said multi-function layer upper surface with an indicia that contains a resin-based colorant/binder.

18. The polymeric sheeting material of claim 17, wherein said multi-function layer is formed from a composition comprising from about 90 to about 100 parts of weight aqueous dispersion of polyurethane, said dispersion comprising about 45 to about 55 parts of water and from about 30 to about 40 parts of aliphatic polyurethane.

19. A frangible, durable, retroreflective polymeric sheeting material, comprising:

a) a frangible multi-function layer of greater than about 6 microns in thickness formed from a composition comprising from about 0 to about 60 parts by weight acrylic emulsion and about 40 to about 100 parts by weight aqueous dispersion of polyurethane, said multi-function layer having a lower surface and an exposed, upper surface;

b) a binder layer comprising synthetic polyester resin crosslinked with a butylated melamine resin attached to said multi-function lower surface;

c) a spacecoat layer comprising polyvinyl butyral under said binder layer;

d) a monolayer of glass microspheres having bottom most and topmost surfaces, said bottommost surfaces embedded in said spacecoat layer and said topmost surfaces embedded in said binder layer;

e) a reflective material underlying said monolayer of glass microspheres; and

f) a pressure sensitive adhesive layer under said reflective material, said polymeric sheeting material being directly thermally print receptive upon said multi-function layer upper surface with an indicia that contains a resin-based colorant/binder.

20. The polymeric sheeting material of claim 19, wherein said multi-function layer is formed from a composition comprising from about 20 to about 50 parts of weight acrylic emulsion and about 40 to about 80 parts by weight aqueous dispersion of polyurethane, said dispersion comprising about 45 to about 55 parts of water and from about 30 to about 40 parts of aliphatic polyurethane.

21. A frangible, durable, retroreflective polymeric sheeting material, comprising:

a) a frangible multi-function layer of greater than about 6 microns in thickness formed from a composition comprising from about 0 to about 60 parts by weight acrylic emulsion and about 40 to about 100 parts by weight aqueous dispersion of polyurethane, said multi-function layer having a lower surface and an upper, exposed surface;

b) a layer comprising polyvinyl butyral attached to said multi-function layer lower surface;

c) a monolayer of glass microspheres embedded in said polyvinyl butyral layer;

d) a reflective material underlying said monolayer of glass microspheres; and

e) a pressure sensitive adhesive layer under said reflective material, said polymeric sheeting material being directly thermally print receptive upon said multi-function layer upper surface using a resin-based colorant/binder.

22. The polymeric sheeting material of claim 21, wherein said multi-function layer is formed from a composition comprising from about 20 to about 50 parts of weight acrylic emulsion and about 40 to about 80 parts by weight aqueous dispersion of polyurethane, said dispersion comprising about 45 to about 55 parts of water and from about 30 to about 40 parts of aliphatic polyurethane.

23. A polymeric sheeting material according to any one of claims 4, 15, 17, 19, or 21, wherein said sheeting is less than about 150 microns in thickness and exhibits residual evidence of physical tampering when a portion of said sheeting experiences a load which creates 25 percent strain of said portion.

24. A polymeric sheeting material according to claim 23, wherein said load at 25 percent strain is less than about 7 pounds.

25. A polymeric sheeting material according to any one of claims 4, 15, 17, 19, or 21, wherein said sheeting is less than about 150 microns in thickness and exhibits residual evidence of physical tampering when a portion of said sheeting experiences a load at break of less than about 7 pounds.

26. A polymeric sheeting material according to any one of claims 12, 15, 17, 19, or 22, said multi-function layer formed from a composition further comprising an ultraviolet light stabilizer and an ultraviolet light absorber, said sheeting being weatherable.

27. A polymeric sheeting material according to any one of claims 12, 15, 17, 19, or 21, further comprising indicia underneath said multi-function layer.

28. A frangible retroreflective polymeric sheeting material, comprising:

a) a frangible topmost layer having a lower surface and an exposed, upper surface, said topmost layer formed from a composition comprising polyethyleneterephthalate and vinylidine chloride/acrylonitrile copolymer;

b) a cover layer attached to said lower surface; and

c) a retroreflective core sheet attached to said cover layer, said retroreflective core sheet having first and second major surfaces, the first major surface of the core sheet being attached to said cover layer, said core sheet comprising in order:

i) a binder layer defining said first major surface of said core sheet;

ii) a spacecoat layer comprising polyvinyl butyral under said binder layer;

iii) a monolayer of microspheres having bottommost and topmost surfaces, said bottommost surfaces imbedded in said spacecoat layer and said topmost surfaces imbedded said binder layer;

iv) a reflective material underlying said monolayer of microspheres; and

v) a pressure sensitive adhesive layer at said bottommost surface underlying said reflective material, said polymeric sheeting material being directly thermally print receptive upon said topmost layer upper surface using resin-based colorant/binder.

29. The polymeric sheeting material of claim 28, wherein said cover layer is less than about 10 microns in thickness and is formed from a composition comprising polyethyleneterephtalate.

30. The polymeric sheeting material of claim 30, wherein said sheeting is less than about 125 microns in a thickness and exhibits residual evidence of physical tampering when a portion of said sheeting experiences a load at break of less than about 15 pounds.

31. The polymeric sheeting material of claim 28, wherein said cover layer is formed from a composition comprising from about 40 to about 100 parts by weight of an aqueous dispersion of aliphatic polyurethane and from about 0 to about 60 parts by weight of an acrylic emulsion.

32. The polymeric sheeting material of claim 31, wherein said cover layer is formed from a composition comprising:

a) from about 45 to about50 parts of an aqueous dispersion of polyurethane, said dispersion comprising from about 45 to about 55 parts of water and from about 30 to about 40 parts of aliphatic polyurethane; and

b) from about 45 to about 50 parts of acrylic emulsion.

33. The polymeric sheeting material of claim 28, further comprising resin-based colorant/binder directly applied to said topmost layer upper surface.

34. The polymeric sheeting material of claim 33, wherein said sheeting comprises a signage article.

35. The polymeric sheeting material of claim 1 or 28 wherein the sheeting is an encapsulated-lens retroreflective sheeting.

36. The polymeric sheeting material of claim 1 or 28 wherein the sheeting is a cube corner element retroreflective sheeting.

37. The polymeric sheeting material of any one of claims 28 or 34, wherein said sheeting is weatherable.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO.: 5,508,105

DATED: April 16, 1996

INVENTOR(S): Bruce D. Orensteen et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In Column 3, Line 7, the word "polyethyleneterephtalate" should read --polyethyleneterephthalate--.

In Column 4, Line 32, the word "polyethyleneterephtalate" should read --polyethyleneterephthalate--.

In Column 4, Line 40, the word "polyethyleneterephtalate" should read --polyethyleneterephthalate--.

In Column 9, Line 5, the last word "pans" should read --parts--.

In Column 9, Line 6, the word "pans" should read --parts--.

In Column 9, Line 8, both words "pans" should read --parts--.

In Column 11, Line 37, the second word "comer" should read --comer--.

In Column 15, Line 35, the word "polyethyleneterephtalate" should read --polyethyleneterephthalate--.

In Column 18, Line 39, the word "robbing" should read --rubbing--.

In Column 26, Line 24, insert --1, -- before the number "12", and the number "22" should read --21--.

In Column 26, Line 29, insert --1, -- before the number "12".

In Column 26, Lines 61-62, the last word "polyethyleneterephtalate" should read --polyethylenterephthalate--.

In Column 26, Line 63, the number "30" should read --29--.

In Column 27, Line 8, insert a space between the word "about" and the number "50".

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,508,105

DATED : April 16, 1996

INVENTOR(S) : Bruce D. Orensteen et al.

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

In Column 28, Line 12, the number "34" should read --33--.

Signed and Sealed this

Fifth Day of November, 1996

Attest:

BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks

United States Patent [19]
Martin

[11] Patent Number: 4,801,193
[45] Date of Patent: Jan. 31, 1989

[54] RETROREFLECTIVE SHEET MATERIAL AND METHOD OF MAKING SAME

[75] Inventor: David C. Martin, Berlin, Conn.

[73] Assignee: Reflexite Corporation, New Britain, Conn.

[21] Appl. No.: 164,184

[22] Filed: Mar. 4, 1988

[51] Int. Cl.[4] G02B 5/124; G02B 5/136
[52] U.S. Cl. 350/103; 350/109; 350/320
[58] Field of Search 350/320, 102, 103, 106, 350/109; 427/166

[56] References Cited

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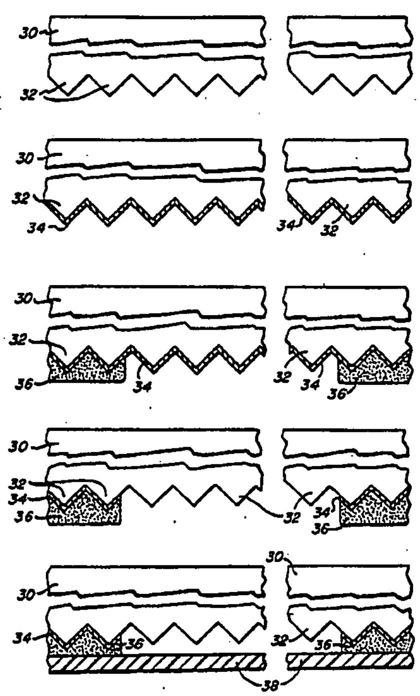
4,637,950	1/1987	Bergeson	350/103
4,703,999	11/1987	Benson	350/103

Primary Examiner—John K. Corbin
Assistant Examiner—Ronald M. Kachmarik

[57] ABSTRACT

A retroreflective sheeting has microretroreflective formations on one surface which are partially metallized and partially exposed to the atmosphere about them. It is produced by forming a coating on microprism surface, and this coating includes a thin metallic deposit over substantially the entire surface and a second coating material over only a portion of the surface. The coated surface is then exposed to a solvent to remove the coating from its predominant area and leave the metal deposit on only a minor portion of the area. A backing sheet is then applied over the microprisms and bonded to the retroreflective sheeting so as to leave an air interface about the predominant area of the microprisms. As a result, some light rays are retroreflected by the metal deposit and some are retroreflected by the atmosphere interface. The sheeting exhibits daytime whiteness over the bulk of its surface area.

24 Claims, 4 Drawing Sheets



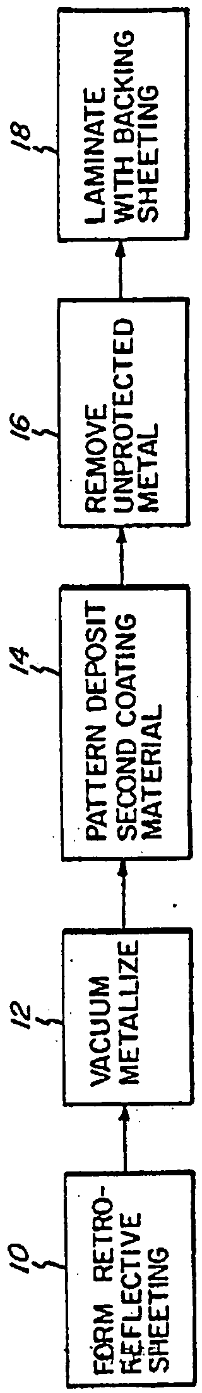

FORM RETRO-REFLECTIVE SHEETING
VACUUM METALLIZE
PATTERN DEPOSIT SECOND COATING MATERIAL
REMOVE UNPROTECTED METAL
LAMINATE WITH BACKING SHEETING
10
12
14
16
18

FIG. 1

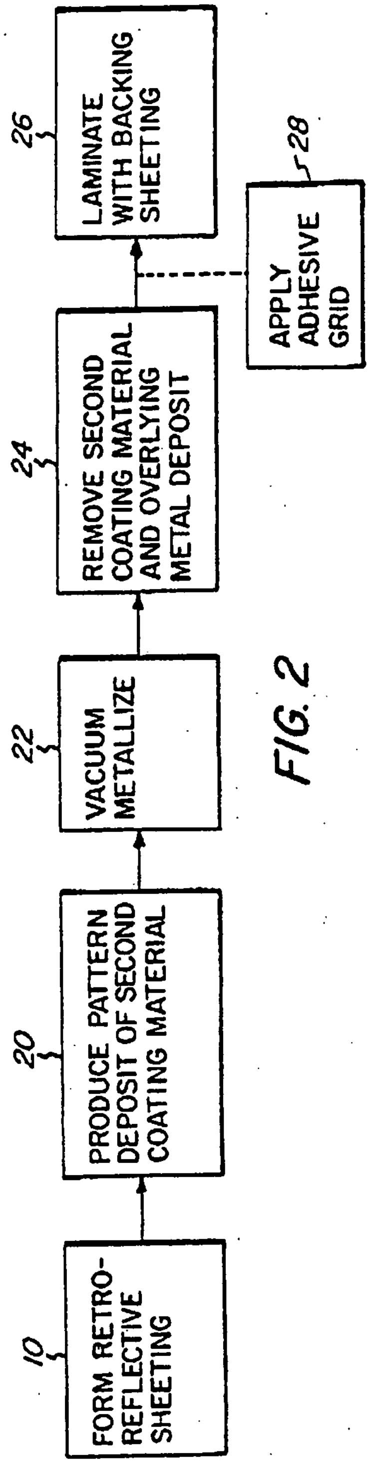

FORM RETRO REFLECTIVE SHEETING
PRODUCE PATTERN DEPOSIT OF SECOND COATING MATERIAL
VACUUM METALLIZE
REMOVE SECOND COATING MATERIAL AND OVERLYING METAL DEPOSIT
LAMINATE WITH BACKING SHEETING
APPLY ADHESIVE GRID
10
20
22
24
26
28

FIG. 2

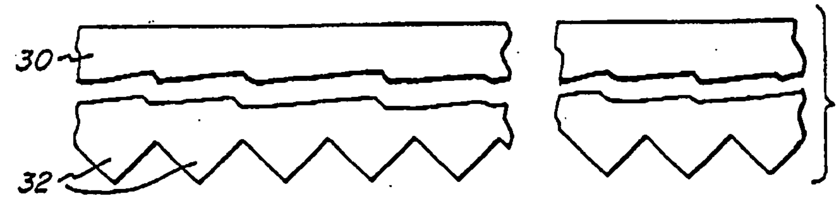


FIG. 3A

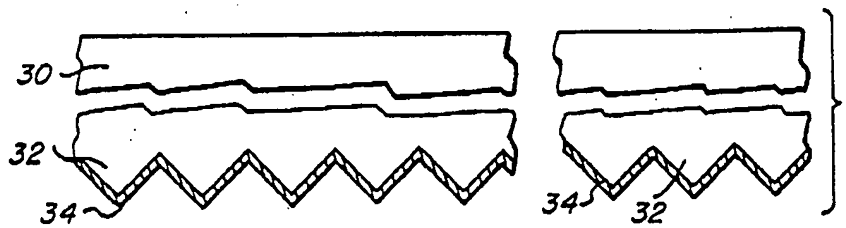


FIG. 3B

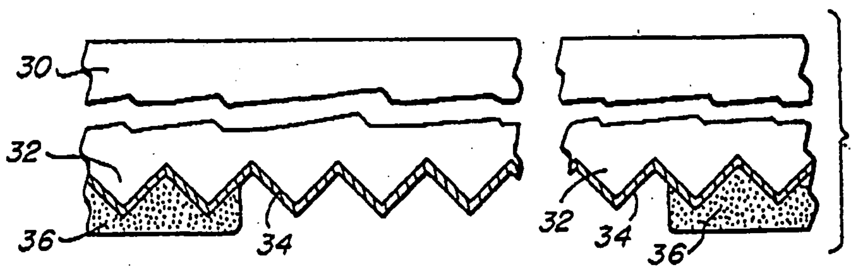


FIG. 3C

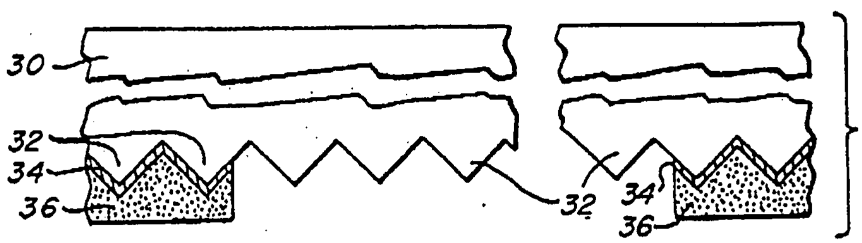


FIG. 3D

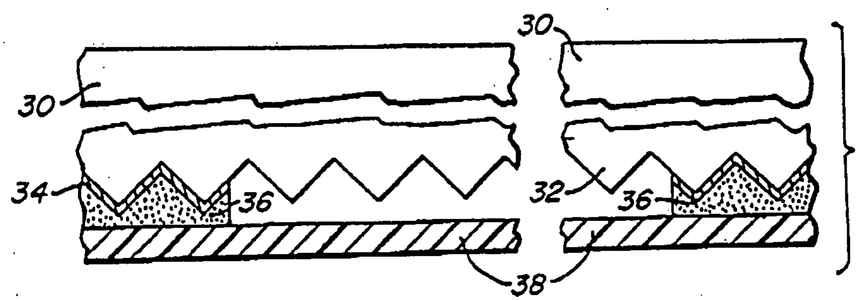


FIG. 3E

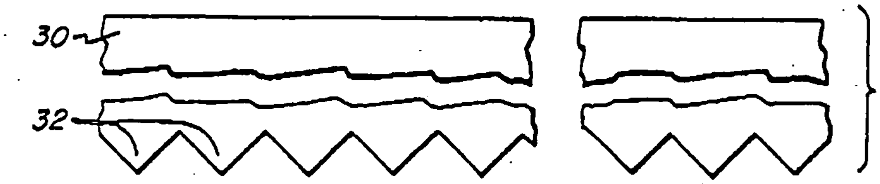


FIG. 4A

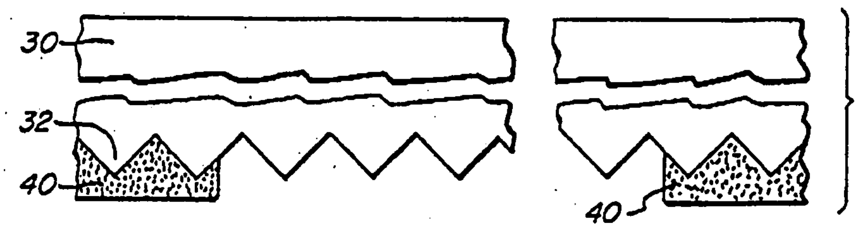


FIG. 4B

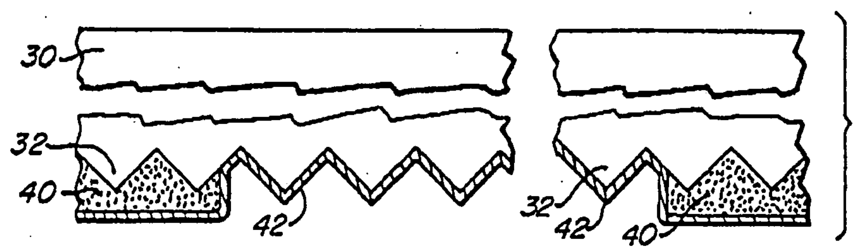


FIG. 4C

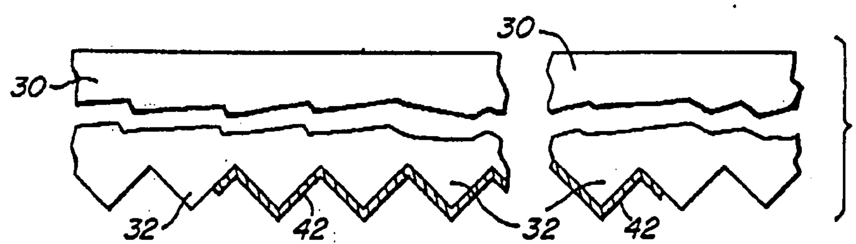


FIG. 4D

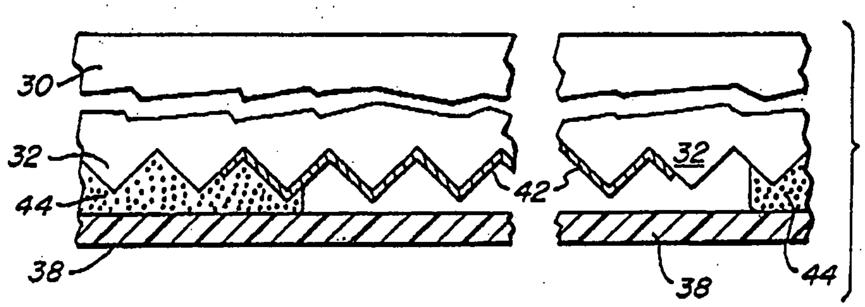


FIG. 4E

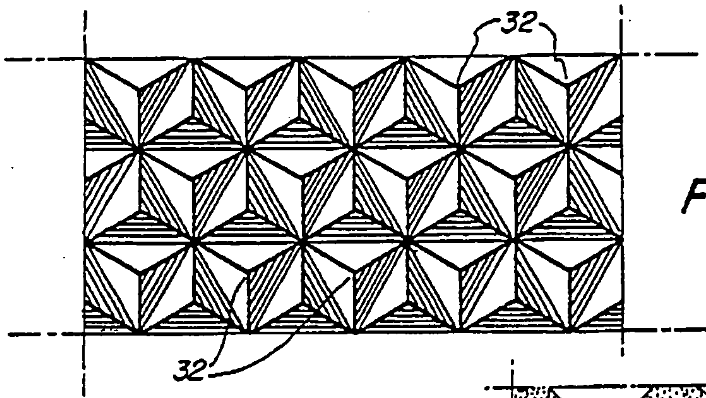


FIG. 6

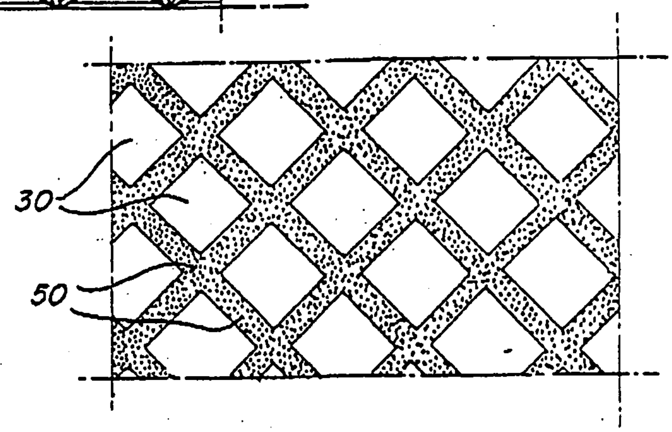


FIG. 5

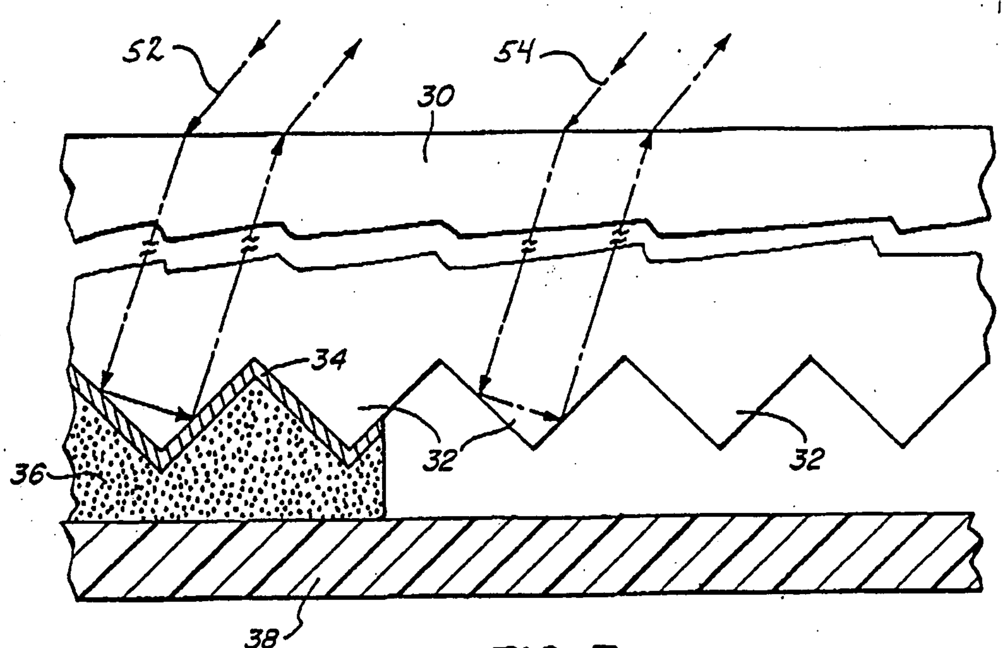


FIG. 7

RETROREFLECTIVE SHEET MATERIAL AND METHOD OF MAKING SAME

BACKGROUND OF THE INVENTION

The present invention relates to retroreflective sheeting employing microprism formations to retroreflect the light rays impinging thereon, and more particularly, to a method for producing such retroreflective sheet material exhibiting a high degree of whiteness and retroreflectivity, and to the sheet materials produced thereby.

Retroreflective sheet material is widely employed for a variety of safety and decorative purposes, and is particularly useful when night time visibility is significant under conditions of low ambient light. In retroreflective materials, the light rays impinging upon the front surface are reflected back towards the source of the illumination in a substantially parallel path. In situations where headlights or search lights, boats and aircraft are the only source of illumination, this ability to retroreflect the bulk of the rays falling thereon is especially significant.

Minnesota Mining and Manufacturing Corporation has manufactured retroreflective sheeting utilizing minute glass beads embedded in a matrix of synthetic resin to provide such retroreflection, and these materials have been sold under the trademark SCOTCHLITE. Illustrative of such materials is Bergeson et al U.S. Pat. No. 4,637,950 granted Jan. 20, 1987.

Applicant's assignee, Reflexite Corporation, has been marketing under the trademark REFLEXITE, reflective sheeting employing microprisms formations to produce such retroreflection. Illustrative of such materials is Rowland U.S. Pat. No. 3,689,346 granted Sept. 5, 1972.

Among the applications for such retroreflective materials are reflective tapes and patches for clothing of firemen, reflective vests and belts, bands for posts and barrels, traffic cone collars, highway signs, warning reflectors, and the like.

It is known that a cube corner prism surrounded by air will retroreflect light incident upon the front surface or base thereof impinging upon and the prism surfaces. However, it is common to coat the prism surfaces with a reflective or specular material such a vacuum deposited aluminum layer to provide a retroreflective interface. In this manner, adhesive and other backing materials may be deposited around the cube corner prisms for lamination to backing sheets and other structures.

Moreover, when using microprisms of less than about 0.010 inch on center spacing, it has been found that there is less retroreflection of light incident at an angle of 30° or more if the surfaces of the microprisms are unmetallized. Thus, when making such microprism sheeting, it is desirable to have some portion of the microprisms coated with a specular material which will have the tendency to reflect light impinging at higher angles of incidence.

The use of a metallized aluminum coating on the prism surfaces tends to produce a grey coloration to the observer in ambient light or daylight conditions. In some applications, this grey appearance is considered aesthetically undesirable.

To prevent or minimize the failure of such retroreflective sheet materials incident to penetration of salt or other corrosive materials, or moisture, about the retroreflective formations, it is common to provide a protective backing over the formations and to seal that backing to the retroreflective sheeting in a grid pattern to produce discrete cells containing isolated clusters of retroreflective formations. Illustrative of such grid structures is Bergeson et al U.S. Pat. No. 4,637,950 granted Jan. 20, 1987.

It is an object of the present invention to provide a novel sealed retroreflective sheeting using microprism formations overlaid by a protective backing element and which exhibits high reflectivity and a desirable degree of whiteness to the observer in daylight.

It is also an object of the present invention to provide such a retroreflective sheet material which may be readily fabricated and which is durable and resistant to the elements. Another object of the present invention is to provide novel methods for fabricating such retroreflective sheet material which are relatively simple and relatively economical, and which produce long-lived materials.

SUMMARY OF THE INVENTION

It has now been found that the foregoing and related objects can be readily attained in a process for producing a retroflective sheeting having microretroreflective formations on one surface which is partially metallized and partially exposed to the atmosphere about them.

A retroreflective sheeting is formed with microretroreflective formations closely spaced about one surface thereof, and these formations are configured to retroreflect light entering the other surface of the sheeting and impinging upon the inner surface of the formations.

A coating comprising a thin metallic deposit is formed on one surface over substantially the entire surface of the formations and a second coating material is formed over only a portion of the formations. The metallic deposit and second coating material are superposed over a portion of the one surface.

A solvent is applied to the one surface to remove the coating from the predominant surface area of the formations. This exposes the surface while leaving a residual coating providing a metal deposit on the surface of the formations over a minor portion of the surface area.

A backing element is adhered to the one surface, and it extends in a plane generally above the formations and is spaced from the predominant surface area of the formations to leave the surface area exposed to the atmosphere thereabout. As a result, light rays entering the other surface of the sheeting and impinging upon the residual coating are reflected thereby, and those impinging upon the exposed surface area are reflected by the interface with the atmosphere.

In one embodiment of the process, the coating step initially deposits metal over substantially the entire area of the one surface and thereafter deposits an organic protective coating material over only a portion thereof. The solvent application step removes the metal deposit in the areas unprotected by the coating material.

Preferably, the organic coating material is applied in a grid pattern, and the coating material is an adhesive and the backing element is bonded thereto. The solvent is a solvent for the metal, the metal is aluminum, and the solvent is an alkali metal hydroxide solution.

In another embodiment of the process, the coating step initially deposits the second coating material over the majority of the area of the one surface with portions of the formations being uncoated thereby. Metal is then

deposited over the entire surface area. The solvent application step removes the coating material, and the metal deposit overlies the coating material to leave the metal deposit in the areas where directly deposited on the surface.

The coating material preferably includes an organic resin, and the solvent may include a solvent for the resin.

The coating material may include magnesium hydroxide or magnesium carbonate hydroxide, and the solvent may be a detergent solution.

The resultant retroreflective sheet material comprises a retroreflective sheeting having a multiplicity of closely spaced microretroreflective formations on one surface thereof with a reflective metal deposit on a minor portion of the area of the one surface. A backing sheeting is adhered to the one surface of the reflective sheeting, and extends in a plane generally above the formation and is spaced from the predominant surface area of the formations. The major area of the one surface is free from the metal deposit and from contact with the backing sheeting to provide an atmospheric interface thereat. The light rays entering the other surface of the sheeting and impinging upon the metal deposit are reflected thereby. Those impinging upon the metal-free surface area are reflected by the atmospheric interface.

Preferably, the coating includes an adhesive superposed on the metal deposit.

The microretroreflective formations are cube corner prisms, and the metal deposit is in a grid-like pattern. The backing sheeting is adhered to the reflective sheet along the grid-like pattern.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagrammatic view of a method for making the improved retroreflective sheeting of the present invention;

FIG. 2 is a diagrammatic view of another embodiment of a method for making the sheeting of the present invention;

FIGS. 3A–3E are diagrammatic views of the reflective sheeting (greatly enlarged) at various points in the process of FIG. 1;

FIGS. 4A–4E are similar diagrammatic views of the reflective sheeting at various points in the process of FIG. 2;

FIG. 5 is a diagrammatic plan view of the sheeting showing a grid pattern for the reflective coating in the sheeting of FIGS. 3 and 4;

FIG. 6 is a plan view to a greatly enlarged scale showing the microprism retroreflective formations; and

FIG. 7 is a diagrammatic view of the reflective sheeting showing the paths of light rays entering through the front surface.

DETAILED DESCRIPTION OF THE ILLUSTRATED EMBODIMENTS

Turning first to FIG. 6 of the attached drawings, therein is illustrated a fragmentary and greatly enlarged plan view of the microprisms 32 which are formed on the rear surface of the retroreflective sheeting. The microprisms are closely spaced and can be described as cube corner formations. Further details concerning the structure and operation of such microprisms may be found in Rowland U.S. Pat. No. 3,684,348 granted Aug. 15, 1972. These microprisms or cube corner formations may have a side edge dimension of up to 0.025 inch, but the preferred structures use edge dimensions of not more than 0.010 inch, and most desirably on the order of 0.004–0.008 inch. The body portion of the sheeting will generally have a thickness on the order of 0.002–0.030 inch and preferably about 0.003–0.010 inch depending upon the method of fabrication, the resins, and the characteristics desired for the retroreflective sheeting.

A particular advantageous method for making such retroreflective sheeting is described and claimed in Rowland U.S. Pat. No. 3,689,346 granted Sept. 5, 1972 in which the cube corner formations are cast in a cooperatively configured mold and are bonded to sheeting which is applied thereover to provide a composite structure in which the cube corner formations project from the one surface of the sheeting.

Another method for fabricating such microprism sheeting is shown in Rowland U.S. Pat. No. 4,244,683 granted Jan. 13, 1981 in which the cube corner formations are produced by embossing a length of sheeting in suitable embossing apparatus with precisely formed molds in a manner which avoids entrapment of air.

As previously indicated, it is customary to provide a backing sheet behind the microprisms so as to protect them and to provide a smooth surface for application of the structure to support surfaces. To effect lamination of such a backing sheet to the retroreflective sheeting, adhesives and ultrasonic welding are generally employed. When adhesives are employed, the adhesives tend to wet the surface of the microprisms and this destroys the air innerface and eliminates their ability to retroreflect. Accordingly, it has been customary to deposit a reflective coating upon the surfaces of the microprisms before the laminating operation, and such reflective coatings have most commonly been vacuum metallized aluminum deposits, although metal lacquers and other specular coating materials have also been used.

It has long been known that the harsh conditions to which the retroreflective material may be exposed in marine and highway applications can produce penetration between the backing sheet and the microprisms. This results in corrosion and delamination of the structure. Thus, it has been common to produce sealed cells of relatively small area by producing a sealing bond between the backing sheet and the retroreflective sheeting. Grid-like patterns to achieve this result are disclosed in Bergeson et al U.S. Pat. No. 4,637,950 granted Jan. 20, 1987.

Turning now to FIGS. 1 and 3, therein illustrated is a preferred method for producing the retroreflective sheeting of the present invention. In the first step shown diagrammatically the box 10 in FIG. 1, the retroreflective sheeting is formed with a body portion 30 with retroreflective formations on the one surface thereof as seen in FIG. 3A. This retroreflective sheeting is then vacuum metallized on its one surface in a vacuum metallizing apparatus designated by the numeral 12 so as to deposit uniformly over the entire surface of the sheeting, a thin deposit 34 of the reflective metal, conventionally aluminum, as seen in FIG. 3B.

In the next step in a coating apparatus 14, the vacuum metallized surface is then printed with a grid-like pattern of a second coating material as indicated by the numeral 36 in FIG. 3C so that, in a grid pattern, there is now a composite of underlying metal deposit 34 and overlying coating material 36.

The coated surface is now subjected to treatment in a solvent both for the deposited metal as shown by the numeral 16 in FIG. 1. That portion of the metal coating 34 which is not protected by the second coating material 36 is removed by the solvent in this step so as to leave the prisms 32 within the areas bounded by the grid free from any coating.

In the last step as indicated by the numeral 18, the backing sheeting 38 is bonded by the coating material 36 to the retroreflective sheeting to produce the composite structure.

Turning now to FIGS. 2 and 4, another embodiment of the method of the present invention is therein illustrated. In the first step designated by the numeral 10 in FIG. 2, the retroreflective sheeting is similarly formed with a body portion 30 and the microprism formations 32. In the second step 20, a coating material 40 is deposited upon the microprism surface of the sheeting on a grid-like pattern.

In the next step indicated by the numeral 22, the sheeting is vacuum metallized to produce a metallic deposit 42 over both the coating 40 and the uncoated prism surfaces.

In the next step designated by the numeral 24, the coated surface is subjected to solvent action which dissolves the second coating material 40, and thereby removes the metal layer 42 lying thereover. This leaves the metallic deposit 42 that has been directly deposited upon the surfaces of the prisms 32.

Although the laminating step 26 may be effected without an adhesive through use of ultrasonic bonding or other suitable techniques, generally it is preferable to produce a grid-like pattern of adhesive 44 on the surface of the retroreflective sheeting and thereafter to bring the backing sheeting 38 into contact therewith to effect the lamination.

In either of the techniques shown in FIGS. 1 and 3, or in FIGS. 2 and 4, the result is that limited areas of the microprisms are coated with the metal deposit, and the predominant surface area of the prisms is free from any coating. The backing sheeting 38 extends in a plane spaced above the prisms 32. As a result, the bulk of the surface area of the microprisms is surrounded by air or other atmosphere.

As seen in FIG. 7, a light ray 52 entering through the front surface of the body portion of the retroreflective sheeting 30 is initially refracted and impinges upon the leftward surface of the microprism 32 and is reflected at a right angle to the rightward surface of the microprism from which it is reflected upwardly and outwardly of the sheeting in a parallel path.

The light ray 54 is similarly refracted when it enters into the sheeting 30, and it impinges upon the leftward prism surface. It is reflected to the rightward prism surface and then reflected outwardly.

In FIG. 5, a grid-like visual pattern produced upon observation of sheeting embodying the present invention will be seen in ambient light. The dark grid pattern represents areas colored grey by the aluminum deposit as seen in the ambient light whereas the lighter areas between the grid lines are characteristic of the uncoated prisms when viewed under ambient light conditions.

Illustrative of the present invention are the following specific examples:

EXAMPLE ONE

Utilizing the method generally illustrated in Rowland U.S. Pat. No. 3,689,346, microprisms having a height of 0.0028 inch and a spacing of 0.006 inch on center were cast upon a polyester film having a thickness of 0.002 inch. The resin employed for the prism was an acrylated epoxy oligomer modified with monofunctional and trifunctional acrylic monomers.

The retroreflective sheeting was vacuum metallized with aluminum to a thickness in excess of 240 Angstroms. The metallized sheeting was then imprinted by a modified gravure roll with a grid pattern of a pressure sensitive, ever-tacky rubber based adhesive sold by B. F. Goodrich under the designation A1569B. The grid has a spacing of ¼ inch between lines and the lines have a thickness of approximately 0.04 inch. Following printing of the grid pattern, the sheeting is passed through a 1.0M. solution of sodium hydroxide for a period of 10–30 seconds during which the unprotected aluminum deposit is removed. The sheeting is then passed through a water bath to rinse the surface, and thence through a dryer. Following drying the sheeting is passed through the nip of a pair of pressure rollers together with a polyethylene backing sheet of 0.001 inch thickness to effect lamination thereof.

The resulting sheet material is found to exhibit excellent weathering characteristics is a weatherometer, excellent retroreflective characteristics, and desirable daytime whiteness.

EXAMPLE TWO

In a process similar to that illustrated in FIG. 2, the retroreflective sheeting described in Example One was initially coated with an offset printing roll to produce a polka dot coating. The composition applied was an aqueous solution of milk of magnesia and a commerically available white latex paint in a ratio of 1:1. After drying, the sheeting was vacuum metallized over the coating with aluminum. Following vacuum metallizing, the sheeting was passed through an aqueous detergent composition which was being rapidly agitated and which removed the coating material initially applied and the aluminum deposited thereover. The sheeting was then rinsed and dried. Upon inspection, approximatley 40% of the surface area was covered by the metallized aluminum deposit.

The retroreflective sheeting was then passed through a grid sealing machine wherein a heat activatable polymeric film of 0.003 inch was grid sealed to the retroreflective sheeting.

Upon inspection, the resultant retroreflective sheet material was found to exhibit good retroreflectivity, good weathering in a weatherometer, and desirable daytime whiteness.

As previously indicated, the microprism sheeting may be formed by casting prisms upon a film service as a body, or by embossing a preformed sheeting, or by casting both body and prisms concurrently. Generally, the resins employed for the microprism sheeting are cross linked thermoplastic formulations, and desirably these resins provide flexibility, light stability, and good weathering characteristics. In some instances, the front face of the retroreflective sheeting may be provided with a protective coating such as by application of a lacquer or other coating material. Suitable resins for the retroreflective sheeting include vinyl chloride, polymers, polycarbonates, methyl methacrylate polymers, polyurethanes and acrylated urethanes.

The backing sheet will also be a flexible, durable polymeric material. Suitable resins include polyethyl-

ene, polypropylene, polyurethanes, acrylated polyurethanes and ethylene/vinyl acetate copolymers.

Although other metals may be used to provide a specular metal deposit including silver, rhodium, copper, tin, zinc, and palladium, the preferred and most economical processes utilize aluminum vacuum deposition. Other deposition techniques include electroless plating, electroplating, ion deposition and sputter coating.

The second coating material utilized in the processes of the present invention will depend upon the process employed and whether adhesive characteristics are desired. In the preferred technique illustrated in FIGS. 1 and 3, the coating material is desirably a pressure sensitive adhesive which will not be unduly affected in the solvent treating step. Preferred adhesives include rubber based systems in solvent carriers and acrylic-based adhesives in solvent systems. Other adhesives may also be employed, and water based systems may also be employed, although sometimes requiring drying time before further processing. Specific examples of suitable adhesive systems are a rubber based, resin modified adhesive sold by B. F. Goodrich under the designation A1569-B, a latex rubber-based adhesive sold by Emhart Industries, Bostik Division, under the designation 8786X and a latex rubber-based system sold by B. F. Goodrich under the designation 26171.

Whether using solvent-based or water based systems, the coating may require drying before further processing. If so, heating may be utilized to accelerate the process.

The second coating material may also be a heat activatable adhesive, or it may be a non-adhesive organic or inorganic coating material. Moreover, the second coating material may be provided by a film of resin, perforated or otherwise formed, so as to encompass only limited portions of the surface.

In the preferred process wherein the metal deposit is to be removed where it is not protected, the solvent conveniently comprises a solution of alkali metal hydroxide or other alkaline solution which will dissolve the aluminum. In the instance of coatings other than metals, solutions with which the metal will react are employed.

In the process illustrated in FIG. 2, the solvent solution is one which will dissolve or remove the second coating material. In some instances, this will be a solvent for the second coating material; and, in other instances, it may be a strong detergent solution accompanied by agitation to lift off the coating material because of its poor bond to the underlying surface.

The step of adhering the backing sheet to the retroreflective sheeting may simply involve passing the adhesive coated retroreflective sheeting through the nip of a pair of rolls together with a backing sheet to apply the necessary pressure to effect adhesion. If a heat activatable adhesive is employed, the retroreflective sheeting may be subjected to preheating prior to passage through the rolls, or the rolls may be heated to achieve the necessary activation. However, it is also practicable to employ ultrasonic welding and other techniques to bond the backing sheet to the retroreflective sheeting by the material of the backing sheet itself.

Where the adhesive coating is applied in the process of FIG. 1 or in the modification of the process of FIG. 2, a grid-like pattern of adhesive may be deposited on the retroreflective sheeting by means of a modified gravure-type roll.

Thus, it can be seen from the foregoing detailed description and attached drawings that the process of the present invention provides a novel retroreflective microprism sheet material exhibiting good daytime whiteness and excellent nighttime retroreflectivity. The material combines retroreflection from metal coated surfaces and air interface surfaces to provide optimum retroreflection over a wide range of angles of incidence. The methods for making the sheeting are relatively simple and economical, and produce material exhibiting long life.

Having thus described the invention, what is claimed is:

1. In a process for producing a retroflective sheeting having microretroreflective formations on one surface which are partially metallized and partially exposed to the atmosphere about them, the steps comprising:

(a) forming a retroreflective sheeting having microretroreflective formations closely spaced on one surface thereof, said formations being configured to retroreflect light entering the other surface of said sheeting and impinging upon the surface of said formations;

(b) forming a coating on said one surface comprising a thin metallic deposit providing a first coating material over substantially the entire surface of said formations and a second coating material over only a portion of said formations, said metallic deposit and second coating material being superposed over a portion of said one surface;

(c) applying a solvent to said one surface to remove said metallic deposit from the major portion of the surface area of said formations and thereby expose the surface thereof where said metallic deposit is removed while leaving a partial coating of said metallic deposit on the surface of said formations over a minor portion of the surface area; and

(d) adhering a backing element to said one surface, said backing element extending in a plane generally above said formations and being spaced from said major portion of said surface area of said formations to leave said surface area exposed to the atmosphere thereabout, whereby light rays entering the said other surface of said sheeting and impinging upon said residual coating are reflected thereby and those impinging upon said exposed surface area are reflected by the interface with the atmosphere.

2. The process in accordance with claim 1 wherein said step of forming a coating comprises initially depositing said metal over substantially the entire area of said one surface and thereafter depositing an organic protective coating material as said second coating material and over only a portion thereof, and wherein said solvent application step removes said metallic deposit in the areas unprotected by said protective coating material.

3. The process in accordance with claim 2 wherein said organic coating material is applied in a grid pattern.

4. The process in accordance with claim 2 wherein said organic protective coating material is an adhesive and said backing element is bonded thereto.

5. The process in accordance with claim 2 wherein said solvent is a solvent for said metal of said metallic deposit.

6. The process in accordance with claim 5 wherein said metal of said metallic deposit is aluminum and wherein said solvent is an alkali metal hydroxide solution.

7. The process in accordance with claim 2 wherein said protective coating material is an adhesive which is applied in a grid pattern over said metallic deposit on said one surface, and wherein said solvent application removes the metallic deposit unprotected thereby, and wherein said backing sheeting is adhered to said retroreflective sheeting in a grid pattern by heat activation of said adhesive.

8. The process in accordance with claim 7 wherein said metal of said metallic deposit is almuminum deposited by vacuum deposition and said aluminum is removed by an alkali metal solution.

9. The process in accordance with claim 1 wherein said step of forming a coating comprises initially depositing said second coating material over the major portion of the area of said one surface with portions of said formations being uncoated thereby, and depositing the metal of said metallic deposit over the entire surface area, and wherein said solvent application step removes said second coating material and the metallic deposit overlying said second coating material to leave said metallic deposit in the areas where directly deposited on said surface.

10. The process in accordance with claim 9 wherein said second coating material includes an organic resin.

11. The process in accordance with claim 9 wherein said solvent is a solvent for said resin.

12. The process in accordance with claim 11 wherein said second coating material includes a magnesium carbonate hydroxide and wherein said solvent is a detergent solution.

13. The process in accordance with claim 9 wherein a said second coating material is water-soluble and is applied to said one surface in a pattern to provide discontinuities in the layer provided thereby.

14. The process in accordance with claim 9 wherein said adhering step includes the deposition of an adhesive to said one surface in a grid-like pattern.

15. A retroreflective sheet material comprising:

(a) retroreflective sheeting having a multiplicity of closely spaced microretroreflective formations on one surface thereof with a coating on a minor portion of said one surface, said coating including a reflective metallic deposit on a minor portion of the area of said one surface; and

(b) backing sheeting adhered to said one surface of said reflective sheeting, and extending in a plane generally above the formations and spaced from the predominant surface area exposed to the atmosphere, the major portion of the area of said one surface being free from said coating and from contact with said backing sheeting to provide an atmosphere interface thereat, whereby light rays entering the said other surface of said sheeting and impinging upon said metallic deposit are reflected thereby and those impinging upon said metal free surface area are reflected by the atmospheric interface.

16. The retroreflective sheet material in accordance with claim 15 wherein said coating includes an adhesive superposed on said metallic deposit.

17. The retroreflective sheet material in accordance with claim 15 wherein said coating includes adhesive disposed on said one surface in a grid-like pattern, and wherein said backing sheeting is adhered to said reflective sheeting along said grid-like pattern.

18. The retroreflective sheet material in accordance with claim 15 wherein said coating is in a grid-like pattern, wherein said metallic deposit is a vacuum metallized deposit of aluminum, and wherein said coating includes a layer of adhesive overlying said aluminum deposit and bonding said backing sheeting to said retroreflective sheeting.

19. The retroreflective sheet material in accordance with claim 18 wherein said formations between the lines of the grid pattern are substantially free from said coating and have an atmospheric interface.

20. The retroreflective sheet material in accordance with claim 15 wherein said coating includes an adhesive disposed on said one surface in a grid-like pattern and wherein a portion of the formations between the lines of said grid-like pattern have said metallic deposit thereon.

21. In a process for producing a retroflective sheeting having microretroreflective formations on one surface which are partially metallized and partially exposed to the atmosphere about them, the steps comprising:

(a) forming a retroreflective sheeting having microretroreflective formations closely spaced on one surface thereof, said formations being configured to retroreflect light entering the other surface of said sheeting and impinging upon the surface of said formations;

(b) forming a coating on said one surface by first depositing a thin metallic deposit providing a first coating material over substantially the entire surface of said formations and thereafter depositing a second coating material on said metallic deposit over only a minor portion of said formations, said second coating material comprising a protective organic adhesive;

(c) applying a solvent for the metal of said metallic deposit to said one surface to remove said metallic deposit in the areas unprotected by said second coating material and thereby from the major portion of the surface area of said formations to expose the surface thereof, said removal leaving a partial coating of said metallic deposit and second coating material on the surface of said formations over a minor portion of the surface area; and

(d) adhering a backing element to said second coating material on said one surface, said backing element extending in a plane generally above said formations and being spaced from said major portion of said surface area of said formations to leave said surface area exposed to the atmosphere thereabout, whereby light rays entering the said other surface of said sheeting and impinging upon said residual coating are reflected thereby and those impinging upon said exposed surface area are reflected by the interface with the atmosphere.

22. In a process for producing a retroreflective sheeting having microretroreflective formations on one surface which are partially metallized and partially exposed to the atmosphere about them, the steps comprising:

(a) forming a retroreflective sheeting having microretroreflective formations closely spaced on one surface thereof, said formations being configured to retroreflect light entering the other surface of said sheeting and impinging upon the surface of said formations;

(b) forming a coating on said one surface by first depositing a second coating material over the major portion of said formations, and thereafter forming a thin metallic deposit comprising a first coating material over substantially the entire sur-

face of said formations, said metallic deposit and second coating material being superposed over only a minor portion of said one surface;

(c) applying a solvent for said second coating material to said one surface to remove said second coating material and the overlying metallic deposit from the major portion of the surface area of said formations and thereby to expose the surface thereof, said metallic deposit remaining on the surface of said formations over a minor portion of the surface area;

(d) depositing an adhesive upon said one surface in a grid-like pattern; and

(e) adhering a backing element to said adhesive on said one surface, said backing element extending in a plane generally above said formations and being spaced from said major portion of said surface area of said formations to leave said surface area exposed to the atmosphere thereabout, whereby light rays entering the said other surface of said sheeting and impinging upon said residual metallic deposit are reflected thereby and those impinging upon said exposed surface area are reflected by the interface with the atmosphere.

23. A retroreflective sheet material comprising:

(a) retroreflective sheeting having a multiplicity of closely spaced microretroreflective formations on one surface thereof with a coating on a minor portion of said one surface, said coating including a reflective metallic deposit on a minor portion of the area of said one surface and an adhesive superposed on said metallic deposit; and

(b) backing sheeting adhered to said adhesive on said one surface of said reflective sheeting, and extending in a plane generally above the formations and spaced from the predominant surface area exposed to the atmosphere, the major portion of the area of said one surface being free from said coating and from contact with said backing sheeting to provide an atmosphere interface thereat, whereby light rays entering the said other surface of said sheeting and impinging upon said metallic deposit are reflected thereby and those impinging upon said metal free surface area are reflected by the atmospheric interface.

24. A retroreflective sheet material comprising:

(a) retroreflective sheeting having a multiplicity of closely spaced microretroreflective formations on one surface thereof with a coating on a minor portion of said one surface, said coating including a reflective metallic deposit and an adhesive disposed in a grid-like pattern, only a minor portion of the surface area of the formations between the lines of said grid-like pattern having said metallic deposit thereon, the major portion of the surface area of said one surface being free from said metallic deposit and said adhesive; and

(b) backing sheeting adhered to said adhesive on said one surface of said reflective sheeting, and extending in a plane generally above the formations and spaced from the predominant surface area exposed to the atmosphere, the major portion of the area of said one surface being free from said coating and from contact with said backing sheeting to provide an atmosphere interface thereat, whereby light rays entering the said other surface of said sheeting and impinging upon said metallic deposit are reflected thereby and those impinging upon said metal free surface area are reflected by the atmospheric interface.

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United States Patent [19]

Bailey

[11] **4,153,412**

[45] **May 8, 1979**

[54] **PROCESS FOR PRINTING REFLECTIVE SHEET MATERIAL**

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[52] **U.S. Cl.** .... **8/2.5 A**; 350/97; 350/105; 428/323

[58] **Field of Search** .... 8/2.5 A; 350/105

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[57] **ABSTRACT**

A process for imparting colored image patterns to an exposed lens retroreflective sheet material comprising disposing a preprinted sublimable-dye source sheet over the exposed lens surface under sufficient pressure to insure intimate contact therebetween, and heating the source sheet to the dye sublimation temperature, whereupon the retroreflective sheet becomes visibly patterned with the pattern on the source sheet.

8 Claims, No Drawings

PROCESS FOR PRINTING REFLECTIVE SHEET MATERIAL

BACKGROUND OF THE INVENTION

This invention relates to providing vivid coloration and graphic intelligence to exposed lens retroreflective sheet constructions, and the resultant constructions.

Exposed lens retroreflective sheet constructions typically contain small spherical lens elements, i.e., small glass microspheres or bends hemispherically embedded in a suitable binder system, and specularly reflecting materials adjacent or on the rear surface of the lens elements, such as disclosed in U.S. Pat. Nos. 3,700,305 and 3,758,192. In use, as light is shined directly on the retroreflective material, the light is reflected back to the source and provides a great deal of illumination to the object containing the retroreflective material thereon. Such materials are commonly used in a variety of constructions, such as street and highway markings, as reflective portions on garments, etc.

The imparting of coloration and graphic intelligence to such retroreflective sheet materials has typically been undertaken by applying some to the backside of the sheet material and using transparent specular reflector and binder material. For example, in U.S. Pat. No. 3,700,305, the specular reflector and binder material can be transparent to light, such that by applying decorative effects to the backside of the sheet material, such effects can be visible under normal light.

Application of coloration via silk screening with colored inks, etc. to the exposed lens surface has been undertaken, but is undesirable in most instances, since retroreflection is virtually eliminated in the inked areas.

In commonly assigned U.S. application Ser. No. 695,974, filed June 14, 1976, there is disclosed a process for printing a colored image-containing transfer layer over a portion of the specularly reflective layer on the spherical lens elements, such that when transfer is undertaken to a substrate, the colored image-containing portions are effectively transferred and are also retroreflective.

It has now been found that a finished non-colored or white exposed lens retroreflective sheeting can be colored or a graphic intelligence imparted thereto by utilization of vapor dye transfer techniques. By utilizing such techniques an end-user can add coloration in-house to the sheeting instead of having to settle for add-on colorations or obtaining same from a supplier's limited selection.

SUMMARY OF THE INVENTION

In accordance with the invention, a process for imparting colored image patterns to exposed lens retroreflective sheet material is provided. Such sheet material comprises a dense monolayer of transparent microspheres partially embedded in, and partially exposed above, a binder composition, with a specularly reflective material disposed adjacent the embedded portions of the microspheres. The binder composition is adapted to receive and retain vapor phase dye stuff throughout its thickness, including portions underlying the microspheres. The process comprises disposing a preprinted sublimable dye-containing source sheet over the exposed lens surface at sufficient pressure to insure intimate contact therebetween, heating the source sheet to the sublimation temperature of the dye, and removing the source sheet, whereby the retroreflective sheet material is visibly patterned with the pattern contained on the dye source sheet. In this manner, vividly colored designs can be applied to retroreflective sheeting.

In the case of reflectorizing a fabric garment, the retroreflective material can be applied to a portion of the fabric from which the garment is made, following which the vapor phase coloring process can be undertaken to impart a uniform visible color pattern to the fabric, including the portion which contains the retroreflective material.

DETAILED DESCRIPTION OF THE INVENTION

The preferred exposed lens retroreflective material useful herein is disclosed in U.S. Pat. No. 3,700,305. The construction therein contains glass beads or microsphere lens elements of from 10 to 200 or more microns diameter (preferably 25 to 75 microns) and has adjacent specularly reflecting material comprising transparent dielectric mirrors. Such dielectric mirrors comprise at least one thin transparent layer having an optical thickness corresponding to an odd-numbered multiple of about one-quarter wavelength of light in the wavelength range of about 3800 to about 10,000 angstroms. The transparent layer has a reflective index of n_1, the faces of the layer being in contact with materials of refracted indices n_2 and n_3, both n_2 and n_3 being at least 0.1 (and preferably at least 0.3) either higher or lower than n_1. Preferably, two or more contiguous transparent layers are utilized to obtain higher reflectivity, each layer being in contact with materials having a refractive index that is at least 0.1 (and preferably 0.3) either higher or lower than the refractive index of the adjacent layers.

The resulting specular reflector comprises an array of materials, in layer form, having an alternating sequence of refractive indices. The various layers are conveniently formed on the glass microspheres subsequent the microspheres having been temporarily substantially hemispherically embedded into a heated plastic coated web, by a vapor deposition in one or more steps to provide the desired number of layers in the alternating sequence of refractive index. Following the buildup of the transparent dielectric mirror materials, the thus-coated glass beads or microspheres are typically coated with an organic resinous binder material, followed by drying or curing, after which an adhesive coating can be overlaid on the binder. The plastic coated web is then removed from the spheres.

Useful materials for providing the transparent layers (generally by vapor deposition), include high-refractive-index materials such as zinc sulfide, zinc selenide, and bizmuth oxide, and low-index materials such as cryolite, magnesium fluoride and silicon dioxide.

While transparent under ordinary diffused lighting conditions, the dielectric mirror also reflects a large enough percentage of light by phase agreement or enhancement of reflection from the interfaces of the transparent layer or layers to provide bright retroreflection of light beamed at the mirror.

While transparency of the specular reflector is preferable, since the coloration as provided by the process of the invention will be more vivid, the invention will also function where a non-transparent reflective layer, e.g., vapor-coated aluminum, is utilized.

An alternative exposed lens retroreflective construction useful in the invention is that disclosed in U.S. Pat. No. 3,758,192. In that construction, the binder material

contains specularly reflective nacreous pigment particles which provide a tangential, preferably contiguous, cup-like surface contact with the under surface of the glass beads to form reflex-reflecting elements therewith.

In the process of the invention, a preprinted sublimable dye-containing source sheet is placed in contact with the exposed microsphere or bead surface under sufficient pressure to insure intimate contact therebetween, typically from about 0.5 to about 10 psi. The sanwich is then heated to the dye sublimation temperature, whereupon the dye effectively transmits into the retroreflective sheet material, in essence transferring to the organic resinous binder material in between each bead. With continued heating, the dye migrates to the back of the bead, but does not interfere with the optical characteristics of the retroreflective construction, i.e., retroreflectivity is not inhibited. The resultant construction is then brightly colored with a solid or graphic pattern having essentially same retroreflective properties as before coloration. For use herein, the term "pattern" corresponds to solid coloration as well as colored graphic images.

Suitable volatilizable dyes are those with sublimation temperatures between about 50° C. and about 250° C. Furthermore, when a garment is the desired end product, the dye should be wash-fast, i.e., not degradable or capable of deterioriating on washing, and should not be degradable when exposed to ultraviolet light. There are many suitable dyes known in the art having these characteristics. They can be generally classified as solvent dyes, disperse dyes, or basic dyes, and have been found useful in transfer printing of textiles such as disclosed in "Dyes For Heat Transfer Printing" by J. Aihara et al, American Dye Stuff Reporter, February, 1975 at pages 46–52. Examples of typical dyes useful in my invention include the following:

YELLOW DYES	
Oil Yellow GR	C.I. 21240
Intratherm Yellow P-345NT	C.I. Disperse Yellow 3
Waxoline Yellow T	C.I.
Irgacet	
Ingracet Yellow 3GCG	C.I. Solvent Yellow 48
Cibacet Yellow GWL	C.I. 10338
Cibacet Golden Yellow 3R	C.I. Disperse Yellow 56
ORANGE DYES	
Brilliant Fast Orange 2R	C.I. Solvent Orange 34
Amasolve Orange EE	C.I. Disperse Orange 3
Dispersol Fast Orange B	C.I. 26080
Cibacet Brown 2RFL	C.I. Disperse Orange 30
Eastman Polyester Orange GR-LSW	C.I. Disperse Orange 57
RED DYES	
Polacet Scarlet GF2R	C.I. Disperse Red 54
Amasolve Scarlet 2B	C.I. Disperse Red 7
Cibacet Red 3BL	C.I. Disperse Red 82
Genacron Pink RL	C.I. Disperse Red 86
Sudan Red GGA	C.I. 21250
VIOLET DYES	
Sudan Irisol	
Eastman Polyester Bordeaux 2B-LSW	C.I. Disperse Violet 44
Amasolve Violet B	C.I. Disperse Violet 27

-continued

Eastman Polyester Rubine R-LSW	C.I. Disperse Violet 42
BLUE DYES	
Colliton Blue Green B	C.I. 62500
Amasolve Blue BG	C.I. Disperse Blue
Cibacet Blue 2R	C.I. 61525
Resoform Blue GL	C.I. 61525
Eastman Fast Blue GLF	C.I. 60767
Genacron Blue BRL	C.I. Disperse Blue 95
GREEN DYES	
Sudan Green 4B	C.I. Solvent Green 3 C.I. 61565
BROWN DYES	
Brilliant Vat Brown FR	C.I. Solvent Brown 9
Latyl Brown MS	C.I. Disperse Brown 2

Other exemplary dyes are provided in American Dye Stuff Reporter, July, 1974 at pages 22–28 and 64; and the Journal of the Society of Dyers and Colorists, December, 1971 at pages 494.

The volatilizable dyes are typically applied to a web such as a sheet, a foil or a woven or non-woven web of synthetic or natural fiber. Preferably, the web consists of paper because the dye has a low affinity of the cellulose therein. The web should be of sufficient thickness to provide dimensional stability to the dye source material during the imaging process.

Printing of the dye itself onto the dye source, i.e., a paper web, is easily accomplished using any of the traditional ink printing methods, e.g., rotogravure, flexography, silk screen, or offset. The ink is normally produced from a dye having suitable aforementioned characteristics and a vehicle to facilitate the application of the dye to the paper. Typically this vehicle is cellulose-based, such as ethyl cellulose or cellulose acetate propionate because of its very low affinity for the volatile dye. Preprinted dye source sheets are commercially available.

The binder material used in the retroreflective sheet construction should be an organic composition in which the sublimed dye is soluble, at sublimation temperatures, without distortion or degradation of the optical qualities of the sheet, and in which the dye can be retained during conditions of light exposure, high heat, and washing (in the case of a garment). Furthermore, the organic binder should be capable of withstanding the dye sublimation temperatures without discoloration and/or excessive softening to the point that the microspheres submerge completely into the binder.

Additionally, the binder must exhibit other properties depending on the ultimate usage of the retroreflective material. For example, if utilized as garment trim, the binder should be relatively soft and flexible, resistant to washing and dry cleaning, reasonably weather resistant, non-toxic, ironable, abrasion-, soil-, and stain-resistant etc. If utilized for outdoor traffic signs, more stringent weatherability criteria would be necessary.

Since the dyes listed above are relatively non-polar, suitable binder materials are relatively non-polar, i.e., they do not contain a predominance of ionic groups therein. Exemplary materials include saturated polyester resins, elastomeric polyurethanes, and polyvinyl chloride resins, although exact selection will in part depend on the ultimate use of the retroreflective material.

In the preferred utility, i.e., as a garment trim, prior art binders have not been found to be able to withstand the dye transfer temperatures without excessive softening, to the point where the glass spheres are forced completely into the binder, the binder thus contacting and adhering to the dye source web. Besides problems with web removal and reduction in retroreflectivity, uniformity of dye transfer in such a situation is extremely poor due to entrapment of air between the source web and the surface of the retroreflective sheeting, preventing effective transfer of the volatilized dye.

One solution has been to utilize resin binder, in a very thin layer, which is too thin to allow complete submergence of the beads therein. A second solution is to utilize crosslinking and/or thermosetting resins to effectively avoid or minimize the softening problems, e.g., isocyanate-crosslinked urethane elastomer resin systems.

In operation, the dye source web is contacted with the top surface of the retroreflective material under sufficient heat and pressure to cause sublimation of the dye into the retroreflective composite. The contact time necessary for production of a visible color or pattern by transfer of sublimed dyes has been ascertained to be from about 2 seconds to about 60 seconds with from about 10 to about 30 seconds being preferred. Decreasing contact times tend to reduce image density and resolution below optimum, whereas contact times greater than about 60 seconds tend to be impractical.

Contact pressures should be sufficient to insure intimate contact and eliminate air between the composite structures to thereby optimize uniformity of the dye transfer. A pressure on the composite of greater than about one-half pound per square inch is adequate for insuring this contact. Increasing pressure up to about 12 pounds per square inch may provide some minor increase in color density, but beyond that point minimal beneficial effect is noted.

The invention will now be more specifically illustrated by the use of the following non-limiting examples, wherein all parts are by weight unless otherwise indicated.

EXAMPLE 1

Transparent glass microspheres having an index of refraction of 1.92 and an average diameter of about 50 microns were cascaded onto a preheated polyethylene coated Kraft paper and the paper then passed through an oven heated to 121° C. for about one and one-half minutes. During passage through the oven the microspheres sank to a depth of about 30 percent of their diameters in the polyethylene layer. A transparent dielectric mirror was prepared as generally described in U.S. Pat. No. 3,700,305 by first vapor depositing a layer of cryolite (Na_3AlF_6) onto the microsphere covered surface of the web in an optical thickness (i.e., the product of physical thickness and index of refraction) corresponding to about one-quarter wavelength of white light, i.e., about one-quarter of 5500 angstroms, which is in the middle of the wavelength spectrum of visible light. Zinc sulfide was then vapor deposited onto the cryolite-coated microsphere surface in an optical thickness again corresponding to about one-quarter wavelength of white light.

A solution was then made from 30 parts of Vitel PE307 resin, tradename for a linear saturated polyester resin made by Goodyear Chemical Co., 35 parts of toluol and 35 parts of cyclohexanone, and 2 parts of Z6040 Silane (tradename of gamma-glycidoxypropyltrimethoxysilane, made by Dow Corning Corp.). This solution was knife coated onto the cryolite and zinc sulfide coated microsphere surface using a knife coater at a coating orifice of 0.006 inch, followed by drying for 5 minutes at 65° C. and 10 minutes at 93° C. The web was then laminated to a backing fabric by placing the coated side of the web in contact with a woven fabric of about 4 ounces per square yard consisting of a 65/35 by weight blend of polyester/cotton fibers and hot laminating, using a Model HP-7 Thermopress, available from the Thermopatch Corp., at about 10 psi pressure and 149° C., for 14 seconds.

After cooling, the polyethylene coated Kraft paper was removed. The white retroreflective fabric construction was then colored by first placing a sample of commercially available printed heat transfer paper, Ortherm Paper available from the Orchard Corp., in contact with the exposed beaded side of the retroreflective fabric construction, then applying about 10 psi pressure and about 204° C. of heat for 45 seconds on a Thermopress. After pressing, the spent dye source web was easily removed and the retroreflective fabric was brightly colored with little or no loss in retroreflective brilliance.

The Z-6040 was utilized to promote adhesion of the binder material to the coated bead surface.

EXAMPLE 2

A sheeting was prepared as per Example 1 up through the zinc sulfide coating. A solution of a thermoset resin system was then prepared consisting of 12 parts Vitel VPE 5545 resin, 18 parts Estane 5703 resin (an elastomeric polyurethane resin made by B. F. Goodrich Chem. Co.), 35 parts methylethylketone, 35 parts dimethyl formamide, 3 parts Cymel 301 (a melamine resin from American Cyanamide), 0.12 parts para toluene sulfonic acid (a catalyst for initiating the melamine crosslinking resin), 2 parts Z6040, and 1.2 parts Desmodur E22 (an aromatic polyisocyanate prepolymer made by Mobay Chem. Corp.). This was then knife coated at a 0.006 inch orifice onto the cryolite and zinc sulfide coated sheet and dried for 5 minutes at 65° C. and 10 minutes at 93° C.

A second solution was knife coated onto the web at an 0.006 inch coating orifice and dried 5 minutes at 65° C. and 10 minutes at 93° C. This solution consisted of 20.2 parts of Estane 5713 resin, 4.8 parts of Rutile titanium dioxide, 23.6 parts of dimethyl formamide, and 51.4 parts of methyl ethyl ketone.

This second coating was utilized as an adhesive system to adhere the retroreflective material to a fabric. The titanium dioxide imparts a white color to the adhesive layer, which when placed behind the transparent binder layer, reinforces the color formed from the sublimation printing step.

This sample was hot laminated to the same fabric used in Example 1. Lamination was undertaken on a Thermopress using about 10 psi pressure for 10 seconds at about 204° C. The polyethylene-coated Kraft paper was then removed and the remaining white retroreflective fabric construction was sublimation printed using the dye source paper of Example 1. The dye source web was placed in contact with the beaded side of the retroreflective fabric construction and the dye transferred by using a Thermopress at about 10 psi pressure for 45 seconds at about 204° C. The spent dye source web was then easily removed and the resultant retroreflective

fabric construction was brightly colored with little or no loss in retroreflective brilliance.

EXAMPLE 3

The retroreflective construction of Example 1 was repeated, and again the construction was laminated to a 4 oz. 65/35 polyester/cotton blend fabric, but only a narrow strip of the retroreflective sheeting was laminated to a much larger piece of fabric. After lamination, the polyethylene coated Kraft paper was removed. The entire portion of fabric (including the narrow strip of retroreflectorized area) was then sublimation printed. After printing, the retroreflectorized area blended into the remainder of the fabric because both the fabric and reflectorized portion were printed with the same pattern held in registry, and both portions retained approximately the same coloration, i.e., the pattern was substantially uniform.

What is claimed is:

1. A process for imparting colored designs to exposed lens retroreflective sheet material, said material comprising

a support film, at least an outer stratum of which is optically clear, a dense monolayer of transparent microspheres partially embedded in, and partially exposed above, said stratum, with a specularly reflective material disposed adjacent the embedded portions of said microspheres, said stratum comprising an organic binder composition adapted to receive and retain vapor phase dyestuff throughout its thickness, including portions underlying the microspheres, without affecting the retroreflectivity of said sheet material, the process comprising:

(a) disposing a preprinted sublimable dye-containing source sheet over the exposed lens surface of said retroreflective sheet materials, and

(b) applying sufficient pressure to said source sheet to insure intimate contact between said retroreflective sheet material and said source sheet, and

(c) applying sufficient heat to said source sheet to cause sublimation of said sublimable dye into said retroreflective sheet, and

(d) removing the source sheet from the retroreflective sheet,

whereupon said retroreflective sheet material becomes visibly patterned with the pattern on the preprinted source sheet.

2. Process of claim 1 wherein said specularly reflective material comprises a coating on said microspheres, said coating comprising a thin transparent layer having a refractive index n_1, the faces of said transparent layer being in contact with materials of refractive index n_2 and n_3, both n_2 and n_3 being at least 0.1 either higher or lower than n_1, and the transparent layer having an optical thickness corresponding to an odd-numbered multiple of about one-quarter wavelength of light in the wavelength range of about 3800 to 10,000 angstroms.

3. The process of claim 1 wherein said binder composition comprises a thermoset resin system.

4. A retroreflective sheet material having visible colored pattern thereon prepared by the process of claim 1.

5. A process for retroreflectorizing a fabric material while not significantly disturbing the appearance of the fabric, comprising

(a) adhering over limited portions of the fabric a retroreflective sheet material that is adherable to the fabric and that comprises

a support film, at least an outer stratum of which is optically clear,

a dense monolayer of transparent microspheres partially embedded in, and partially exposed above, said stratum, and

a specularly reflective material disposed adjacent the embedded portions of said microspheres, said stratum comprising an organic binder composition adapted to receive and retain vapor phase dye stuff throughout its thickness, including portions underlying the microspheres, without affecting the retroreflectivity of said sheet material, and

(b) disposing a preprinted sublimable dye-containing source sheet against said fabric, such that the source sheet overlies portions of the fabric covered by said retroreflective sheet material and surrounding portions of the fabric, and

(c) applying sufficient pressure to said source sheet to insure intimate contact between said source sheet and said fabric, and

(d) applying sufficient heat to said source sheet to cause sublimiation of said sublimable dye into said fabric,

whereupon the retroreflective sheet material and surrounding fabric become visibly patterned with the pattern of the source sheet.

6. A fabric having retroreflective portions thereon and a colored design prepared by the process of claim 5.

7. The process of claim 5 wherein said specularly reflective material comprises a coating on said microspheres, said coating comprising a thin transparent layer having a refractive index n_1, the faces of said transparent layer being in contact with materials of refractive index n_2 and n_3, both n_2 and n_3 being at least 0.1 either higher or lower than n_1, and the transparent layer having an optical thickness corresponding to an odd-numbered multiple of about one-quarter wavelength of light in the wavelength range of about 3800 to 10,000 angstroms.

8. The process of claim 5 wherein said binder composition comprises a thermoset resin system.

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